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INVESTIGATIONS OF AEROSOL PARTICLE - VAPOR
INTERACTIONS FOR PESTICIDES AND OTHER
HIGH MOLECULAR WEIGHT ORGANICS

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VAPOR PRESSURE ESTIMATES OF INDIVIDUAL
POLYCHLORINATED BIPHENYLS AND COMMERCIAL
FLUIDS USING GAS CHROMATOGRAPHIC RETENTION DATA

INTRODUCTION

Predicting contaminant transport, distribution, and fate in the environment relies on accurate physical and chemical properties for developing suitable models. Required vapor pressure and water solubility data are lacking, or are in some cases questionable, particularly for components of complex mixtures.

Only limited vapor pressure data are available for polychlorinated biphenyls (PCB), an important class of organic pollutants. Up to a few years ago, the only vapor pressure information was for Aroclor fluids, determined in the 150–300°C range by Monsanto Corporation (1). Mackay and Wolkoff (2) extrapolated these data to estimate Aroclor vapor pressures at 25°C, which today are the most widely quoted volatility data for PCB fluids. Aroclor mixtures contain fifty or more components and the vapor pressures referenced above are dominated by a few of the more volatile PCB.

Of the 209 possible PCB, vapor pressures of only a few have been directly measured by physical methods (effusion, gas saturation, or extrapolation from boiling point data). Recently, Bidleman (3) estimated the liquid phase vapor pressures (P_L^0) at 25°C of 30 PCB using a capillary gas chromatographic (GC) method. This chapter describes the use of this GC determined vapor pressure data set in conjunction with published retention indices of PCB to estimate the liquid phase vapor pressures of 134 PCB found in five Aroclor fluids.

METHOD

In 1977, Albro and coworkers (4) computed retention indices (RI) for all of the 209 possible PCB and biphenyl on 13 GC liquid phases, including 3% Dexsil-410 and 10% OV-101 at 200°C. Albro and Parker (5) subsequently determined the composition of the PCB mixtures Aroclor 1016 and 1242 using 12 packed columns containing different GC phases. In 1981, Albro et al. (6) used a capillary Dexsil-410 column to determine RI at 200°C and molar percentages of all the PCB components in Aroclors 1248, 1254 and 1260.

$-\log P_L^0$ at 25°C was plotted versus RI at 200°C for the 30 PCB and biphenyl whose P_L^0 had been determined by capillary GC, using RI data on Dexsil-410 and OV-101 phases. The Dexsil-410 RI were the experimental values of Albro et al. (6) for 23 of the PCB, and those calculated from the half-index table of Albro et al. (4) for the remaining 7 and biphenyl. RI for the 30 PCB and biphenyl on OV-101 were calculated using the half-index table.

Linear regression equations were fitted to these two plots using 27 of the PCB, with biphenyl and the three monochlorobiphenyls being excluded (see DISCUSSION section). From these two equations, estimates of P_L^0 at 25°C for 134 PCB found in Aroclors 1016, 1242, 1248, 1254, and 1260 were calculated using the published RI values.

The partial pressures ($P_{L,i}$) of individual PCB in each fluid were calculated using the percent composition information of Albro et al. (5,6) assuming Raoult's Law:

$$P_{L,i} = P_{L,i}^{\circ} X_i \quad (\text{Equation 1})$$

where $P_{L,i}^{\circ}$ is the P_L° for the pure component, and X_i is the mole fraction of an individual PCB in the fluid. Vapor pressures of the five Aroclors were estimated by summing the partial pressures of individual PCB in each fluid.

DISCUSSION

Retention Index Correlated Vapor Pressures of Individual PCB

The $-\log P_L^{\circ}$ versus RI correlation plot for data on the intermediate polarity Dexsil-410 phase is shown in Figure 1. A similar plot using RI data on the non-polar OV-101 phase is presented in Figure 2. Both of these plots reveal a marked discontinuity which occurs between the mono- and dichlorobiphenyls. Biphenyl and the three monochlorobiphenyls are shifted off a line passing through the di- to heptachlorobiphenyls. The reason for this deviation is not completely understood, however the discrepancies are not likely to be due to inaccuracies in P_L° , since the capillary GC measured P_L° (3) agreed well with the literature values for these compounds (Table I). Because of this obvious discontinuity only the di- to heptachlorobiphenyl points were used in calculating the $-\log P_L^{\circ}$ versus RI regression equations.

A good fit ($r^2 = 0.996$) was obtained using the Dexsil-410 RI data with the model:

$$-\log P_L^{\circ} = (-3.974 \times 10^{-3}) \text{ RI} + 4.434 \quad (\text{Equation 2})$$

Further improvement was obtained ($r^2 = 0.999$) with the model:

$$-\log P_L^O = (-4.189 \times 10^{-3}) RI + 4.184 \quad (\text{Equation 3})$$

using the RI data on OV-101. Vapor pressure estimates of the 134 PCB found in five Aroclor fluids were calculated using these two equations and the RI data of Albro et al. (4,6) (Table I). Vapor pressure estimates of the other 75 PCB not found in the Aroclor fluids can be obtained by using Equation 2 or 3 and the half index table of Albro et al. (4).

P_L^O values obtained by correlation from the two sets of RI data differed on the average by 22.7% and in the worst case (decachlorobiphenyl) by a factor of 2.4, with the heavier PCB exhibiting a slightly greater overall difference. These differences were due to changes in elution order for some PCB on the two liquid phases.

Within a given series of isomers, P_L^O generally increased with the number of ortho-chlorines. This "ortho-effect" produces large differences in volatilities of PCB having the same chlorine content as observed by Bidleman (3). Mullin et al. (7) also found that retention times of isomeric PCB increased with decreasing number of ortho-substituted chlorines.

Accuracy of RI-Correlated Vapor Pressures

Vapor pressures of only a few PCB have been measured by methods other than GC. Boiling point data (8,9) were extrapolated to estimate vapor pressures of 2-chlorobiphenyl, 4-chlorobiphenyl, 2,5-dichlorobiphenyl, and 2,4,6-

trichlorobiphenyl. The resulting vapor pressures at 25°C were P_L^O since extrapolations were made from above the melting points. Vapor pressures of the crystalline solids (P_S^O) at 25°C were determined by effusion (10) for 2,2'-dichlorobiphenyl and 4,4'-dichlorobiphenyl, and by gas saturation (11,12) for 2,5,2',5'-tetrachlorobiphenyl, 2,4,5,2',5'-pentachlorobiphenyl, 4-chlorobiphenyl, 2,3,5,6,2',3',5',6'-octachlorobiphenyl, and decachlorobiphenyl. For these, P_L^O were estimated from P_S^O using (13):

$$\ln P_L^O/P_S^O = 6.8 (T_m - 298)/298 \quad (\text{Equation 4})$$

where T_m is the melting point (Kelvin). The resulting P_L^O for the above PCB and the average of several experimental results for biphenyl (3) are listed in Tables I and II under "Literature Value".

Average PCB P_L^O from OV-101 and Dexsil-410 correlations are compared with literature values in Table II. In all cases but one, the correlated results are slightly higher. The worst agreements occur with 2,5-dichlorobiphenyl and 2,4,6-trichlorobiphenyl, for which the correlated P_L^O are 3.0 and 4.1 times higher than P_L^O estimated from boiling point data. However the extrapolated P_L^O at 25°C were based on only three boiling points above 100°C, and thus their accuracies are uncertain. Including the two worst cases, the average agreement between correlated and literature P_L^O was about a factor of two.

The 95% confidence intervals of P_L^O (Figure 1 and Table II) were calculated using the method described in Draper and

Smith (14). Confidence bands for the OV-101 plot were very narrow (Table II), and these bands were omitted from Figure 2 for clarity. Since GC-determined P_L^O were available only up to the heptachlorobiphenyls, extrapolation was necessary to calculate P_L^O for the octa- through decachlorobiphenyls, and whether linearity holds in this region remains uncertain. However the fairly good agreement between predicted and literature P_L^O for the one octachlorobiphenyl and decachlorobiphenyl (Table II) suggests the same level of accuracy for the other octa- and nonachlorobiphenyls.

Vapor Pressures of Aroclor Fluids

Partial pressures ($P_{L,i}$) of individual PCB found in the five Aroclors were estimated by assuming that the solutions behaved ideally. $P_{L,i}$ for di- through nonachlorobiphenyls were calculated using Dexsil-410 correlated P_L^O and are presented in Table III. $P_{L,i}$ values computed using OV-101 correlated P_L^O are presented in Table IV. $P_{L,i}$ of biphenyl and the monochlorobiphenyls (Tables III and IV) were calculated using literature P_L^O (Table I). No entry in Tables III and IV indicates that either the PCB was not found in the Aroclor fluid, or that its $P_{L,i}$ contribution to the overall vapor pressure was insignificant ($<10^{-9}$ torr). Vapor pressures of the Aroclor fluids are largely dominated by a small number of PCB in each mixture. The high partial pressures of some PCB are due to high vapor pressures and/or large mole fractions.

Vapor pressures of each Aroclor fluid were calculated by summing the partial pressures of individual PCB found in

the fluid. Resulting overall vapor pressures for Aroclors 1016, 1242, 1248, 1254, and 1260 are presented in Table V, along with Aroclor vapor pressures calculated by extrapolation of Monsanto data (1) from 150-300°C to 25°C using the Antoine equation by Mackay and Wolkoff (2).

Aroclor vapor pressures calculated using Dexsil-410 and OV-101 correlated P_L^0 values exhibited good agreement, and decreased in the order 1016 > 1242 > 1248 > 1254 > 1260. The values reported by Mackay and Wolkoff (2) decreased in the order 1248 > 1242 > 1254 > 1260, with 1016 not reported. The higher vapor pressure reported (2) for 1248 versus 1242 is surprising, especially considering the predominance of more volatile mono-, di- and trichlorobiphenyls in Aroclor 1242 (Tables III and IV). The reason for this discrepancy may be due to the data originally published by Monsanto (1). Monsanto reported the Aroclor vapor pressure order 1242 > 1248 > 1254 > 1260 at 100°C, with the Aroclor 1242, 1254, and 1260 vapor pressure versus 1/T plots exhibiting very similar slopes. However, the Aroclor 1248 slope was different (1), and as a consequence when the data were extrapolated to 25°C by Mackay and Wolkoff (2) the 1248 vapor pressure was higher.

Vapor pressures of Aroclors 1248, 1254, and 1260 were approximately 2.4 - 3.3 times lower than values previously reported by Mackay and Wolkoff (Table V). The lower values found here may be due to several reasons:

1. Extrapolation of vapor pressures from high temperature data using the Antoine equation tends to over-

estimate the vapor pressure (13), and thus the values reported by Mackay and Wolkoff (2) may be too high.

2. There is no experimental evidence to support ideal behavior of Aroclor fluids. Therefore in the calculation of PCB partial pressures, the assumption that these solutions behave ideally has possibly resulted in an underestimation of the Aroclor vapor pressures. According to Reid et al. (15) vapor pressures calculated using Raoult's Law generally are lower than those determined experimentally, since activity coefficients are usually greater than unity. Eggertsen et al. (16) also cited deviation from ideal solution behavior as a factor which may influence the accuracy of the GC method for estimating vapor pressures of petroleum distillate fractions.

3. Differences in composition of technical PCB mixtures are known to exist and have been reported in the literature (17,18).

CONCLUSIONS

The vapor pressure data reported in this study are useful from two aspects. First, vapor pressure estimates are now available for all the PCB found in commercial Aroclor fluids. When modeling PCB transport phenomena, such as air/water exchange and adsorption to airborne particles, it is the individual PCB vapor pressures which are needed. Second, calculations of vapor pressures for the commercial fluids show which PCB in the mixtures dominate the "overall" vapor pressure. It is these components that are most likely

to be enriched in gaseous PCB emissions from spills and disposal sites.

The approach used in this study shows promise in estimating the volatilities of other complex mixtures from known vapor pressures of a limited number of components in the mixture, coupled with gas chromatographic retention data.

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TABLE I

VAPOR PRESSURES OF INDIVIDUAL PCB FOUND IN AROCLOR FLUIDS

		$-\log P_L^0$ (torr, 25°C)				
IUPAC No.	Chlorine Substitution Pattern	OV-101 RI	Dexsil 410 RI	GC	Literature	
		<u>Correlation</u>	<u>Correlation</u>	<u>Method</u> ^a	<u>Value</u>	<u>Ref.</u>
0	Biphenyl			1.304	1.376	3
Monochlorobiphenyls						
1	2			1.782	1.860	8
2	3			2.126		
3	4			2.156	2.167 ^c	
Dichlorobiphenyls						
4	2,2'	2.611	2.600		2.650	10
6	2,3'	2.887	2.918			
7	2,4	2.803	2.791	2.739		
8	2,4'	2.929	2.970			
9	2,5	2.761	2.759	2.860	3.237	9
10	2,6	2.598	2.556			
11 ^b	3,3'	3.164	3.244	3.167		
12	3,4	3.231	3.331			
13	3,4'	3.205	3.299			
14	3,5	3.025	3.057			
15	4,4'	3.247	3.355	3.237	3.485	10

TABLE I (continued)

		$-\log P_L^O$ (torr, 25°C)			
IUPAC No.	Chlorine Substitution Pattern	OV-101 RI Correlation	Dexsil 410 RI Correlation	GC Method ^a	Literature Value Ref.
Trichlorobiphenyls					
16	2,3,2'	3.394	3.347		
17	2,4,2'	3.277	3.256		
18	2,5,2'	3.235	3.204		
19	2,6,2'	3.071	3.009		
20	2,3,3'	3.670	3.729		
22	2,3,4'	3.712	3.764		
25	2,4,3'	3.553	3.562		
26	2,5,3'	3.511	3.510		
27	2,6,3'	3.348	3.327		
28	2,4,4'	3.595	3.593		
29 ^b	2,4,5	3.469	3.458	3.478	
30 ^b	2,4,6	3.080	2.993	3.056	3.648 9
31	2,5,4'	3.553	3.586	3.520	
32	2,6,4'	3.390	3.375		
33	3,4,2'	3.704	3.784		
35	3,4,3'	3.980	4.102		
37	3,4,4'	4.022	4.150		
39	3,5,4'	3.817	3.884		

TABLE I (continued)

		$-\log P_L^O$ (torr, 25°C)				
Chlorine						
IUPAC	Substitution	OV-101 RI	Dexsil 410 RI	GC	Literature	
No.	Pattern	Correlation	Correlation	Method ^a	Value	Ref.
Tetrachlorobiphenyls						
40	2,3,2',3'	4.177	4.190	4.134		
41	2,3,4,2'	4.085	4.134			
42	2,3,2',4'	4.060	4.062			
43	2,3,5,2'	3.905	3.844			
44	2,3,2',5'	4.018	4.011			
45	2,3,6,2'	3.771	3.697			
46	2,3,2',6'	3.855	3.812			
47	2,4,2',4'	3.943	3.931			
48	2,4,5,2'	3.943	3.911			
49	2,4,2',5'	3.901	3.915			
52	2,5,2',5'	3.859	3.888	3.844	4.108	11
53	2,5,2',6'	3.696	3.605	3.688		
54	2,6,2',6'	3.532	3.411			
55	2,3,4,3'	4.362	4.460			
56	2,3,3',4'	4.487	4.611			
60	2,3,4,4'	4.403	4.508			
66	2,4,3',4'	4.370	4.420	4.335		
70	2,5,3',4'	4.328	4.384	4.353		
71	2,6,3',4'	4.165	4.182			
72	2,5,3',5'	4.123	4.130			
74	2,4,5,4'	4.261	4.285			
75	2,4,6,4'	3.871	3.820			
76	3,4,5,2'	4.345	4.496			
77	3,4,3',4'	4.797	4.965	4.809		

TABLE I (continued)

		$-\log P_L^O$ (torr, 25°C)				
Chlorine						
IUPAC	Substitution	OV-101 RI	Dexsil 410 RI	GC	Literature	
No.	Pattern	Correlation	Correlation	Method ^a	Value	Ref.
78	3,4,5,3'	4.621	4.810			
79	3,4,3',5'	4.592	4.690			
80	3,5,3',5'	4.387	4.416			
81	3,4,5,4'	4.663	4.865			
Pentachlorobiphenyls						
83	2,3,5,2',3'	4.688	4.643			
84	2,3,6,2',3'	4.554	4.480			
85	2,3,4,2',4'	4.751	4.786			
87	2,3,4,2',5'	4.709	4.738	4.770		
91	2,3,6,2',4'	4.437	4.301			
92	2,3,5,2',5'	4.529	4.464			
95	2,3,6,2',5'	4.395	4.253			
97	2,4,5,2',3'	4.726	4.702			
98	2,4,6,2',3'	4.336	4.249			
99	2,4,5,2',4'	4.609	4.551	4.658		
101	2,4,5,2',5'	4.567	4.519	4.560	4.627	11
102	2,4,5,2',6'	4.403	4.301			
103	2,4,6,2',5'	4.177	4.074			
105	2,3,4,3',4'	5.178	5.294	5.170		
106	2,3,4,5,3'	4.986	5.020			
108	2,3,4,3',5'	4.973	5.052			
110	2,3,6,3',4'	4.864	4.825			
113	2,3,6,3',5'	4.659	4.559			
114	2,3,4,5,4'	5.028	5.064			

TABLE I (continued)

		$-\log P_L^O$ (torr, 25°C)				
Chlorine						
IUPAC	Substitution	OV-101 RI	Dexsil 410 RI	GC	Literature	
No.	Pattern	Correlation	Correlation	Method ^a	Value	Ref.
118	2,4,5,3',4'	5.036	5.108	5.047		
120	2,4,5,3',5'	4.831	4.817			
121	2,4,6,3',5'	4.441	4.341			
122	3,4,5,2',3'	5.128	5.278			
123	3,4,5,2',4'	5.011	5.127			
126	3,4,5,3',4'	5.438	5.668			
127	3,4,5,3',5'	5.233	5.394			
Hexachlorobiphenyls						
128	2,3,4,2',3',4'	5.560	5.660	5.592		
131	2,3,4,6,2',3'	5.023	4.905			
132	2,3,4,2',3',6'	5.245	5.167			
133	2,3,5,2',3',5'	5.199	5.084			
134	2,3,5,6,2',3'	5.036	4.857			
135	2,3,5,2',3',6'	5.065	4.861			
136	2,3,6,2',3',6'	4.931	4.659			
138	2,3,4,2',4',5'	5.417	5.429	5.397		
143	2,3,4,5,2',6'	5.170	5.143			
146	2,3,5,2',4',5'	5.237	5.143			
148	2,3,5,2',4',6'	4.847	4.682			
149	2,3,6,2',4',5'	5.103	4.925	4.968		
151	2,3,5,6,2',5'	4.877	4.718			
153	2,4,5,2',4',5'	5.275	5.215	5.280		
154	2,4,5,2',4',6'	4.885	4.778			
156	2,3,4,5,3',4'	5.803	5.922	5.793		

TABLE I (continued)

		$-\log P_L^0$ (torr, 25°C)				
Chlorine						
IUPAC	Substitution	OV-101 RI	Dexsil 410 RI	GC	Literature	
No.	Pattern	Correlation	Correlation	Method ^a	Value	Ref.
157	2,3,4,3',4',5'	5.819	6.022			
158	2,3,4,6,3',4'	5.333	5.473			
163	2,3,5,6,3',4'	5.346	5.433			
167	2,4,5,3',4',5'	5.677	5.747			
168	2,4,6,3',4',5'	5.287	5.330			
Heptachlorobiphenyls						
170	2,3,4,5,2',3',4'	6.184	6.216	6.202		
171	2,3,4,6,2',3',4'	5.715	5.624	5.752		
174	2,3,4,5,2',3',6'	5.870	5.755			
176	2,3,4,6,2',3',6'	5.400	5.179			
177	2,3,5,6,2',3',4'	5.727	5.596			
179	2,3,5,6,2',3',6'	5.413	5.123			
180	2,3,4,5,2',4',5'	6.041	5.970	6.013		
181	2,3,4,5,6,2',4'	5.660	5.501			
182	2,3,4,5,2',4',6'	5.652	5.573			
183	2,3,4,6,2',4',5'	5.572	5.418			
185	2,3,4,5,6,2',5'	5.618	5.445			
186	2,3,4,5,6,2',6'	5.455	5.247			
187	2,3,5,6,2',4',5'	5.585	5.366	5.640		
188	2,3,5,6,2',4',6'	5.195	4.949			
189	2,3,4,5,3',4',5'	6.443	6.606			
190	2,3,4,5,6,3',4'	6.087	5.958			
192	2,3,4,5,6,3',5'	5.882	5.728			
193	2,3,5,6,3',4',5'	5.987	6.181			

TABLE I (continued)

Chlorine		$-\log P_L^O$ (torr, 25°C)				
IUPAC	Substitution	OV-101 RI	Dexsil 410 RI	GC	Literature	
No.	Pattern	Correlation	Correlation	Method ^a	Value	Ref.
Octachlorobiphenyls						
194	2,3,4,5,2',3',4',5'	6.808	6.872			
195	2,3,4,5,6,2',3',4'	6.469	6.252			
196	2,3,4,5,2',3',4',6'	6.339	6.200			
197	2,3,4,6,2',3',4',6'	5.870	5.807			
198	2,3,4,5,6,2',3',5'	6.289	6.037			
199	2,3,4,5,6,2',3',6'	6.154	5.902			
200	2,3,4,6,2',3',5',6'	5.882	5.604			
201	2,3,4,5,2',3',5',6'	6.351	6.125			
202	2,3,5,6,2',3',5',6'	5.895	5.533		5.306	12
203	2,3,4,5,6,2',4',5'	6.326	6.105			
204	2,3,4,5,6,2',4',6'	5.937	5.684			
205	2,3,4,5,6,3',4',5'	6.728	6.661			
Nonachlorobiphenyls						
206	2,3,4,5,6,2',3',4',5'	7.093	6.940			
207	2,3,4,5,6,2',3',4',6'	6.624	6.427			
208	2,3,4,5,6,2',3',5',6'	6.636	6.304			
209	Decachlorobiphenyl	7.378	7.003		7.414	12

^a Average of P_L^O values determined on Apolane 87 and BP-1 liquid phases using the GC method of Bidleman (Reference 3).

^b Not found in Aroclor fluids.

^c Average of values reported in References 8 and 12.

TABLE II

COMPARISON OF PCB VAPOR PRESSURES CALCULATED USING RI
CORRELATION WITH VALUES REPORTED IN THE LITERATURE

		P_L^O (torr, 25°C) and 95% confidence limits		
Compound		P_L^O	Confidence Limits	
			lower	upper
2,2'				
	OV-101	2.4×10^{-3}	1.9×10^{-3}	3.2×10^{-3}
	Dexsil-410	2.5×10^{-3}	1.4×10^{-3}	4.4×10^{-3}
	Literature value	2.2×10^{-3}		
2,5				
	OV-101	1.7×10^{-3}	1.3×10^{-3}	2.3×10^{-3}
	Dexsil-410	1.7×10^{-3}	1.0×10^{-3}	3.0×10^{-3}
	Literature value	5.8×10^{-4}		
4,4'				
	OV-101	5.7×10^{-4}	4.4×10^{-4}	7.3×10^{-4}
	Dexsil-410	4.4×10^{-4}	2.6×10^{-4}	7.6×10^{-4}
	Literature value	3.3×10^{-4}		
2,4,6				
	OV-101	8.3×10^{-4}	6.4×10^{-4}	1.1×10^{-3}
	Dexsil-410	1.0×10^{-3}	5.8×10^{-4}	1.8×10^{-3}
	Literature value	2.2×10^{-4}		
2,5,2',5'				
	OV-101	1.4×10^{-4}	1.1×10^{-4}	1.8×10^{-4}
	Dexsil-410	1.3×10^{-4}	7.6×10^{-5}	2.2×10^{-4}
	Literature value	7.8×10^{-5}		
2,4,5,2',5'				
	OV-101	2.7×10^{-5}	2.1×10^{-5}	3.5×10^{-5}
	Dexsil-410	3.0×10^{-5}	1.8×10^{-5}	5.2×10^{-5}
	Literature value	2.4×10^{-5}		
2,3,5,6,2',3',5',6'				
	OV-101	1.3×10^{-6}	9.8×10^{-7}	1.6×10^{-6}
	Dexsil-410	2.9×10^{-6}	1.7×10^{-6}	5.0×10^{-6}
	Literature value	4.9×10^{-6}		
Decachlorobiphenyl				
	OV-101	4.2×10^{-8}	3.1×10^{-8}	5.6×10^{-8}
	Dexsil-410	9.9×10^{-8}	5.5×10^{-8}	1.8×10^{-7}
	Literature value	3.8×10^{-8}		

TABLE III

PARTIAL PRESSURES OF INDIVIDUAL PCB IN AROCLOR FLUIDS FROM
DEXSIL 410 RETENTION INDEX CORRELATION DATA.

IUPAC	Chlorine		$P_{L,i}$ (10^{-6} torr, 25°C)				
	Substitution						
No.	Pattern		<u>1016</u>	<u>1242</u>	<u>1248</u>	<u>1254</u>	<u>1260</u>
0	Biphenyl		210.36 ^a	4.21 ^a			
Monochlorobiphenyls							
1	2		110.43 ^a	93.87 ^a			
2	3		7.48 ^a	2.99 ^a			
3	4		68.08 ^a	14.98 ^a			
Dichlorobiphenyls							
4	2,2'		109.52	100.22	6.28		
6	2,3'		16.55	14.98	8.33	0.85	
7	2,4		18.77	16.83			
8	2,4'		110.37	96.12	1.93		
9	2,5		5.92	5.40			
10	2,6		5.56	3.61			
12	3,4		0.51	0.42			
13	3,4'		0.60	0.60			
14	3,5		3.24	3.07			
15	4,4'		4.72	4.37			

TABLE III (continued)

IUPAC	Chlorine		$P_{L,i}$ (10^{-6} torr, 25°C)				
	Substitution						
No.	Pattern		<u>1016</u>	<u>1242</u>	<u>1248</u>	<u>1254</u>	<u>1260</u>
Trichlorobiphenyls							
16	2,3,2'		15.74	14.62	3.78		
17	2,4,2'		17.42	16.20	1.05		
18	2,5,2'		67.96	58.52	62.20	0.44	
19	2,6,2'		10.58	9.50			
20	2,3,3'		7.45	6.79			
22	2,3,4'		4.82	4.55	2.13		
25	2,4,3'		4.91	4.61			
26	2,5,3'		1.92	1.70	2.32		
27	2,6,3'		2.73	2.54			
28	2,4,4'		36.96	33.95			
31	2,5,4'		12.24	11.75	24.15	1.87	
32	2,6,4'		9.74	9.07	6.16		
33	3,4,2'		5.06	4.65			
35	3,4,3'		0.30	0.52			
37	3,4,4'		1.34	1.15	0.91	0.14	0.064
39	3,5,4'		1.41	1.34			

TABLE III (continued)

Chlorine		$P_{L,i}$ (10^{-6} torr, 25°C)				
IUPAC	Substitution					
No.	Pattern	1016	1242	1248	1254	1260
Tetrachlorobiphenyls						
40	2,3,2',3'	0.12	0.097	0.72	0.17	0.026
41	2,3,4,2'	1.47	1.23			
42	2,3,2',4'			6.11	1.89	0.57
43	2,3,5,2'	0.67	0.63			
44	2,3,2',5'	1.11	1.03			
45	2,3,6,2'	2.01	1.81	11.51	0.30	
46	2,3,2',6'	0.51	0.48			
47	2,4,2',4'	2.12	1.93	3.73	0.61	0.094
48	2,4,5,2'	1.73	1.63			
49	2,4,2',5'	4.23	3.99	4.63	1.98	0.53
52	2,5,2',5'	5.63	5.28	10.82	5.64	2.47
53	2,5,2',6'	2.66	2.41	15.64	0.32	
54	2,6,2',6'	0.74	0.66			
55	2,3,4,3'			0.038	0.15	0.042
56	2,3,3',4'		0.15		0.044	0.007
60	2,3,4,4'		0.065			
66	2,4,3',4'	0.053	0.31	1.88	0.85	0.084
70	2,5,3',4'		0.46	2.63	1.96	0.35
71	2,6,3',4'			0.43		
72	2,5,3',5'		0.24	1.56	0.75	0.21
74	2,4,5,4'	0.70	1.05	0.13	0.16	0.047
75	2,4,6,4'	3.63	3.30			
76	3,4,5,2'				0.057	0.003
77	3,4,3',4'		0.037	0.051	0.013	0.004

TABLE III (continued)

IUPAC	Chlorine	$P_{L,i}$ (10^{-6} torr, 25°C)				
	Substitution					
No.	Pattern	1016	1242	1248	1254	1260
78	3,4,5,3'		0.081			
79	3,4,3',5'		0.049		0.047	0.008
80	3,5,3',5'					
81	3,4,5,4'		0.038			
Pentachlorobiphenyls						
83	2,3,5,2',3'				0.073	0.020
84	2,3,6,2',3'	0.003	0.13	0.23	0.57	0.23
85	2,3,4,2',4'		0.065	0.090	0.35	0.051
87	2,3,4,2',5'		0.016	0.19	0.70	0.20
91	2,3,6,2',4'			0.89	2.50	1.61
92	2,3,5,2',5'		0.041	0.069	0.22	0.072
95	2,3,6,2',5'	0.10	0.30			
97	2,4,5,2',3'			0.15	0.51	0.12
98	2,4,6,2',3'	0.022	0.073			
99	2,4,5,2',4'		0.15	0.71	1.71	0.23
101	2,4,5,2',5'		0.082	0.45	2.11	1.53
102	2,4,5,2',6'					
103	2,4,6,2',5'			1.59	0.24	0.084
105	2,3,4,3',4'		0.013			
106	2,3,4,5,3'				0.038	0.006
108	2,3,4,3',5'	0.014	0.041	0.002	0.049	0.012
110	2,3,6,3',4'			0.25	1.27	0.53
113	2,3,6,3',5'	0.003	0.11	0.86		0.003
114	2,3,4,5,4'				0.022	0.003

TABLE III (continued)

IUPAC	Chlorine	$P_{L,i}$ (10^{-6} torr, 25°C)				
	Substitution					
No.	Pattern	1016	1242	1248	1254	1260
118	2,4,5,3',4'				0.63	0.16
120	2,4,5,3',5'		0.047		0.023	0.46
121	2,4,6,3',5'		0.42	1.97	1.60	0.26
122	3,4,5,2',3'				0.040	0.099
123	3,4,5,2',4'		0.027			
126	3,4,5,3',4'		0.001		0.003	0.034
127	3,4,5,3',5'		0.002			
Hexachlorobiphenyls						
128	2,3,4,2',3',4'				0.029	0.010
131	2,3,4,6,2',3'				0.017	0.001
132	2,3,4,2',3',6'				0.14	0.19
133	2,3,5,2',3',5'			0.093	0.002	0.005
134	2,3,5,6,2',3'			0.015	0.053	0.14
135	2,3,5,2',3',6'				0.027	0.040
136	2,3,6,2',3',6'			0.044	0.074	0.24
138	2,3,4,2',4',5'		0.003	0.007	0.15	0.19
143	2,3,4,5,2',6'		0.005			
146	2,3,5,2',4',5'				0.054	0.11
148	2,3,5,2',4',6'					
149	2,3,6,2',4',5'			0.091	0.43	1.13
151	2,3,5,6,2',5'				0.063	0.011
153	2,4,5,2',4',5'		0.001	0.008	0.20	0.50
154	2,4,5,2',4',6'					0.023
156	2,3,4,5,3',4'					0.005
157	2,3,4,3',4',5'				0.002	

TABLE III (continued)

IUPAC	Chlorine		$P_{L,i}$ (10^{-6} torr, 25°C)				
	Substitution						
No.	Pattern	1016	1242	1248	1254	1260	
158	2,3,4,6,3',4'				0.015	0.006	
163	2,3,5,6,3',4'						
167	2,4,5,3',4',5'				0.004	0.003	
168	2,4,6,3',4',5'			0.026	0.20	0.028	
Heptachlorobiphenyls							
170	2,3,4,5,2',3',4'				0.003	0.004	
171	2,3,4,6,2',3',4'				0.007	0.10	
174	2,3,4,5,2',3',6'					0.002	
176	2,3,4,6,2',3',6'			0.006		0.038	
177	2,3,5,6,2',3',4'						
179	2,3,5,6,2',3',6'				0.042	0.062	
180	2,3,4,5,2',4',5'				0.008	0.077	
181	2,3,4,5,6,2',4'				0.009	0.086	
182	2,3,4,5,2',4',6'					0.013	
183	2,3,4,6,2',4',5'				0.044	0.098	
185	2,3,4,5,6,2',5'				0.040	0.20	
186	2,3,4,5,6,2',6'					0.021	
187	2,3,5,6,2',4',5'				0.021	0.048	
188	2,3,5,6,2',4',6'			0.13	0.008	0.007	
189	2,3,4,5,3',4',5'						
190	2,3,4,5,6,3',4'						
192	2,3,4,5,6,3',5'				0.004	0.018	
193	2,3,5,6,3',4',5'					0.015	

TABLE III (continued)

IUPAC	Chlorine		$P_{L,i}$ (10^{-6} torr, 25°C)				
	Substitution						
No.	Pattern	<u>1016</u>	<u>1242</u>	<u>1248</u>	<u>1254</u>	<u>1260</u>	
Octachlorobiphenyls							
194	2,3,4,5,2',3',4',5'						0.003
195	2,3,4,5,6,2',3',4'						
196	2,3,4,5,2',3',4',6'						0.005
197	2,3,4,6,2',3',4',6'						0.005
198	2,3,4,5,6,2',3',5'				0.009		0.001
199	2,3,4,5,6,2',3',6'						0.005
200	2,3,4,6,2',3',5',6'						0.004
201	2,3,4,5,2',3',5',6'						0.012
202	2,3,5,6,2',3',5',6'						0.009
203	2,3,4,5,6,2',4',5'						0.001
204	2,3,4,5,6,2',4',6'						0.003
205	2,3,4,5,6,3',4',5'						
Nonachlorobiphenyls							
206	2,3,4,5,6,2',3',4',5'						0.001
207	2,3,4,5,6,2',3',4',6'						0.004
208	2,3,4,5,6,2',3',5',6'						0.001

^a These partial pressures were calculated from literature P_L^O values (Table I).

TABLE IV

PARTIAL PRESSURES OF INDIVIDUAL PCB IN AROCLOR FLUIDS FROM
OV-101 RETENTION INDEX CORRELATION DATA.

Chlorine		$P_{L,i}$ (10^{-6} torr, 25°C)				
IUPAC	Substitution					
No.	Pattern	1016	1242	1248	1254	1260
0	Biphenyl	210.36 ^a	4.21 ^a			
Monochlorobiphenyls						
1	2	110.43 ^a	93.87 ^a			
2	3	7.48 ^a	2.99 ^a			
3	4	68.08 ^a	14.98 ^a			
Dichlorobiphenyls						
4	2,2'	106.78	97.72	6.12		
6	2,3'	17.77	16.09	8.95	0.91	
7	2,4	18.26	16.37			
8	2,4'	121.29	105.63	2.12		
9	2,5	5.89	5.37			
10	2,6	5.05	3.28			
11	3,3', ^b					
12	3,4	0.65	0.53			
13	3,4'	0.75	0.75			
14	3,5	3.49	3.30			
15	4,4'	6.06	5.61			

TABLE IV (continued)

Chlorine		$P_{L,i}$ (10^{-6} torr, 25°C)				
IUPAC	Substitution					
<u>No.</u>	<u>Pattern</u>	<u>1016</u>	<u>1242</u>	<u>1248</u>	<u>1254</u>	<u>1260</u>
Trichlorobiphenyls						
16	2,3,2'	14.13	13.12	3.39		
17	2,4,2'	16.59	15.43	1.00		
18	2,5,2'	63.27	54.48	57.92	0.41	
19	2,6,2'	9.17	8.24			
20	2,3,3'	8.53	7.78			
22	2,3,4'	5.43	5.12	2.41		
25	2,4,3'	5.01	4.70			
26	2,5,3'	1.91	1.70	2.31		
27	2,6,3'	2.60	2.42			
28	2,4,4'	36.79	33.79			
29	2,4,5 ^b					
30	2,4,6 ^b					
31	2,5,4'	13.21	12.68	26.06	2.01	
32	2,6,4'	9.41	8.76	5.95		
33	3,4,2'	6.09	5.59			
35	3,4,3'	0.40	0.69			
37	3,4,4'	1.80	1.54	1.22	0.19	0.086
39	3,5,4'	1.65	1.57			

TABLE IV (continued)

IUPAC	Chlorine	$P_{L,i}$ (10^{-6} torr, 25°C)				
	Substitution					
No.	Pattern	<u>1016</u>	<u>1242</u>	<u>1248</u>	<u>1254</u>	<u>1260</u>
Tetrachlorobiphenyls						
40	2,3,2',3'	0.12	0.10	0.74	0.17	0.027
41	2,3,4,2'	1.64	1.37			
42	2,3,2',4'			6.14	1.90	0.57
43	2,3,5,2'	0.58	0.55			
44	2,3,2',5'	1.09	1.02			
45	2,3,6,2'	1.69	1.52	9.71	0.25	
46	2,3,2',6'	0.46	0.43			
47	2,4,2',4'	2.06	1.88	3.63	0.59	0.091
48	2,4,5,2'	1.61	1.52			
49	2,4,2',5'	4.37	4.12	4.78	2.05	0.55
52	2,5,2',5'	6.02	5.64	11.57	6.03	2.64
53	2,5,2',6'	2.15	1.95	12.69	0.26	
54	2,6,2',6'	0.56	0.50			
55	2,3,4,3'			0.048	0.19	0.052
56	2,3,3',4'		0.19		0.059	0.010
60	2,3,4,4'		0.083			
66	2,4,3',4'	0.060	0.34	2.11	0.96	0.094
70	2,5,3',4'		0.52	3.00	2.23	0.40
71	2,6,3',4'			0.44		
72	2,5,3',5'		0.25	1.58	0.76	0.21
74	2,4,5,4'	0.74	1.12	0.14	0.16	0.049
75	2,4,6,4'	3.23	2.93			
76	3,4,5,2'				0.081	0.004
77	3,4,3',4'		0.054	0.075	0.019	0.006

TABLE IV (continued)

IUPAC	Chlorine	$P_{L,i}$ (10^{-6} torr, 25°C)				
	Substitution					
No.	Pattern	<u>1016</u>	<u>1242</u>	<u>1248</u>	<u>1254</u>	<u>1260</u>
78	3,4,5,3'		0.12			
79	3,4,3',5'		0.061		0.059	0.010
80	3,5,3',5'					
81	3,4,5,4'		0.061			
Pentachlorobiphenyls						
83	2,3,5,2',3'				0.066	0.018
84	2,3,6,2',3'	0.003	0.11	0.20	0.48	0.19
85	2,3,4,2',4'		0.071	0.098	0.38	0.055
87	2,3,4,2',5'		0.018	0.21	0.74	0.21
91	2,3,6,2',4'			0.65	1.83	1.18
92	2,3,5,2',5'		0.035	0.059	0.19	0.062
95	2,3,6,2',5'	0.072	0.21			
97	2,4,5,2',3'			0.15	0.49	0.12
98	2,4,6,2',3'	0.018	0.060			
99	2,4,5,2',4'		0.13	0.62	1.50	0.20
101	2,4,5,2',5'		0.073	0.41	1.89	1.37
102	2,4,5,2',6'					
103	2,4,6,2',5'			1.26	0.19	0.066
105	2,3,4,3',4'		0.017			
106	2,3,4,5,3'				0.041	0.006
108	2,3,4,3',5'	0.017	0.049	0.002	0.058	0.015
110	2,3,6,3',4'			0.23	1.16	0.49
113	2,3,6,3',5'	0.002	0.085	0.68		0.002
114	2,3,4,5,4'				0.023	0.003

TABLE IV (continued)

Chlorine		$P_{L,i}$ (10^{-6} torr, 25°C)				
IUPAC	Substitution					
No.	Pattern	1016	1242	1248	1254	1260
118	2,4,5,3',4'				0.74	0.18
120	2,4,5,3',5'		0.046		0.022	0.44
121	2,4,6,3',5'		0.33	1.56	1.27	0.21
122	3,4,5,2',3'				0.057	0.14
123	3,4,5,2',4'		0.035			
126	3,4,5,3',4'		0.001		0.006	0.058
127	3,4,5,3',5'		0.003			
Hexachlorobiphenyls						
128	2,3,4,2',3',4'				0.036	0.013
131	2,3,4,6,2',3'				0.013	0.001
132	2,3,4,2',3',6'				0.11	0.16
133	2,3,5,2',3',5'			0.071	0.002	0.004
134	2,3,5,6,2',3'			0.010	0.035	0.093
135	2,3,5,2',3',6'				0.017	0.025
136	2,3,6,2',3',6'			0.023	0.040	0.13
138	2,3,4,2',4',5'		0.003	0.007	0.16	0.19
143	2,3,4,5,2',6'		0.005			
146	2,3,5,2',4',5'				0.043	0.086
148	2,3,5,2',4',6'					
149	2,3,6,2',4',5'			0.061	0.28	0.75
151	2,3,5,6,2',5'				0.044	0.008
153	2,4,5,2',4',5'		0.001	0.007	0.18	0.44
154	2,4,5,2',4',6'					0.018
156	2,3,4,5,3',4'					0.006
157	2,3,4,3',4',5'				0.003	

TABLE IV (continued)

IUPAC	Chlorine		$P_{L,i}$ (10^{-6} torr, 25°C)				
	Substitution						
No.	Pattern	1016	1242	1248	1254	1260	
158	2,3,4,6,3',4'				0.021	0.008	
163	2,3,5,6,3',4'						
167	2,4,5,3',4',5'				0.004	0.004	
168	2,4,6,3',4',5'			0.029	0.22	0.030	
Heptachlorobiphenyls							
170	2,3,4,5,2',3',4'				0.003	0.004	
171	2,3,4,6,2',3',4'				0.006	0.083	
174	2,3,4,5,2',3',6'					0.001	
176	2,3,4,6,2',3',6'			0.004		0.023	
177	2,3,5,6,2',3',4'						
179	2,3,5,6,2',3',6'				0.022	0.032	
180	2,3,4,5,2',4',5'				0.007	0.065	
181	2,3,4,5,6,2',4'				0.006	0.059	
182	2,3,4,5,2',4',6'					0.010	
183	2,3,4,6,2',4',5'				0.031	0.069	
185	2,3,4,5,6,2',5'				0.027	0.14	
186	2,3,4,5,6,2',6'					0.013	
187	2,3,5,6,2',4',5'				0.012	0.029	
188	2,3,5,6,2',4',6'			0.008	0.004	0.004	
189	2,3,4,5,3',4',5'						
190	2,3,4,5,6,3',4'						
192	2,3,4,5,6,3',5'				0.003	0.013	
193	2,3,5,6,3',4',5'					0.024	

TABLE IV (continued)

IUPAC	Chlorine		$P_{L,i}$ (10^{-6} torr, 25°C)				
	Substitution						
No.	Pattern		<u>1016</u>	<u>1242</u>	<u>1248</u>	<u>1254</u>	<u>1260</u>
Octachlorobiphenyls							
194	2,3,4,5,2',3',4',5'						0.003
195	2,3,4,5,6,2',3',4'						
196	2,3,4,5,2',3',4',6'						0.004
197	2,3,4,6,2',3',4',6'						0.004
198	2,3,4,5,6,2',3',5'					0.005	0.001
199	2,3,4,5,6,2',3',6'						0.003
200	2,3,4,6,2',3',5',6'						0.002
201	2,3,4,5,2',3',5',6'						0.007
202	2,3,5,6,2',3',5',6'						0.004
203	2,3,4,5,6,2',4',5'						
204	2,3,4,5,6,2',4',6'						0.001
205	2,3,4,5,6,3',4',5'						
Nonachlorobiphenyls							
206	2,3,4,5,6,2',3',4',5'						
207	2,3,4,5,6,2',3',4',6'						0.003
208	2,3,4,5,6,2',3',5',6'						

^a These partial pressures were calculated from literature

P_L^O values (Table 1).

^b Not found in Aroclor fluids.



TABLE V

VAPOR PRESSURES OF AROCLOR FLUIDS

<u>Aroclor Fluid</u>	<u>P_L (torr, 25°C)</u>		
	Dexsil-410 RI	OV-101 RI	Mackay & Wolkoff
	<u>Correlation</u>	<u>Correlation</u>	<u>(Reference 2)</u>
1016	9.01×10^{-4}	9.05×10^{-4}	Not reported
1242	5.72×10^{-4}	5.76×10^{-4}	4.06×10^{-4}
1248	1.87×10^{-4}	1.80×10^{-4}	4.94×10^{-4}
1254	3.26×10^{-5}	3.18×10^{-5}	7.71×10^{-5}
1260	1.37×10^{-5}	1.24×10^{-5}	4.05×10^{-5}



Fig. 1. Plot of $-\text{Log } P_L^0$ (torr, 25°C) vs. retention index (RI) at 200°C on Dexsil-410 liquid phase. Solid = regression line, dotted = 95% confidence interval for single predicted P_L^0 from published RI values. ■ = biphenyl and 3 monochlorobiphenyls (not included in regression), ● = di- through heptachlorobiphenyls.

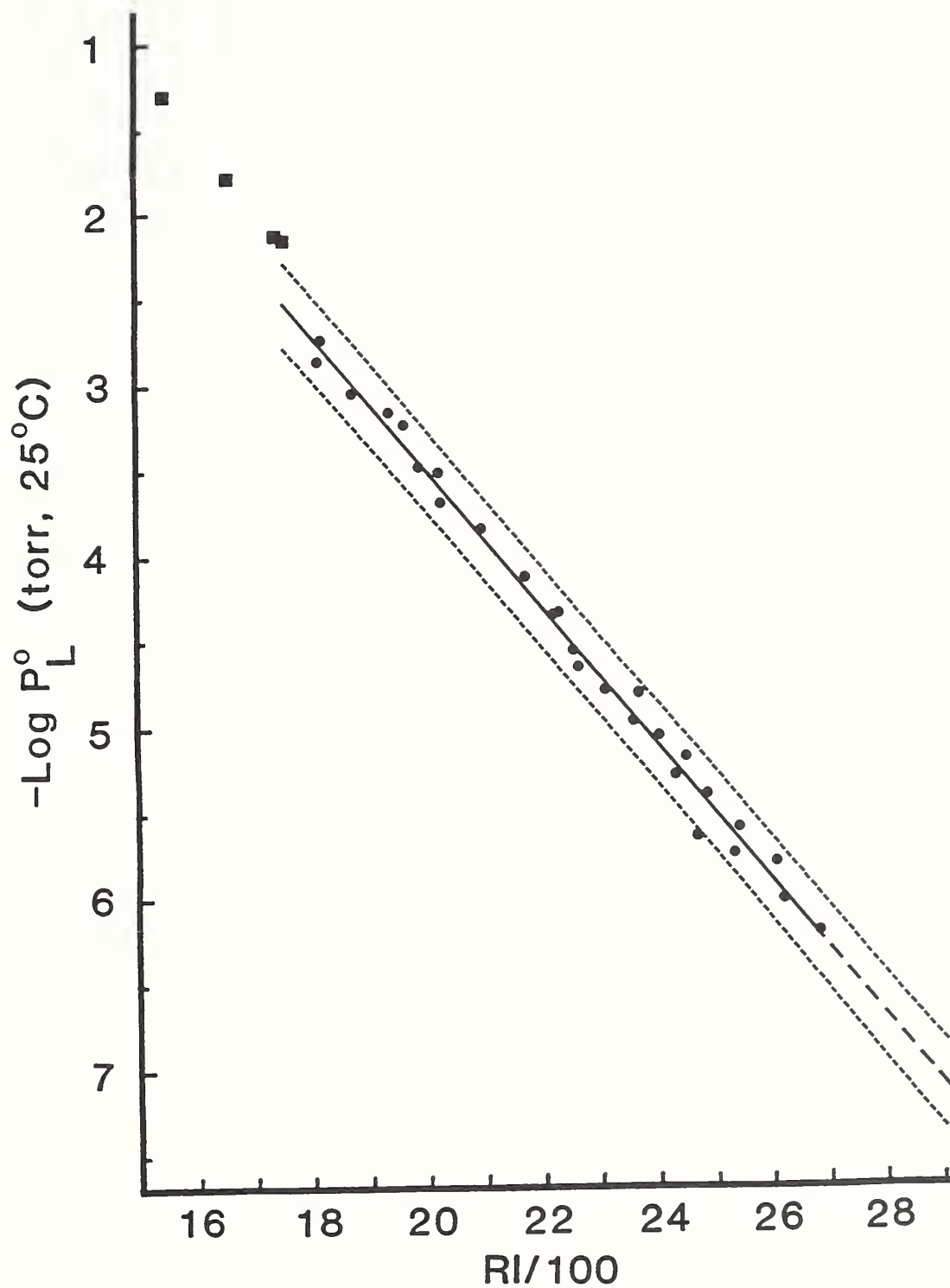
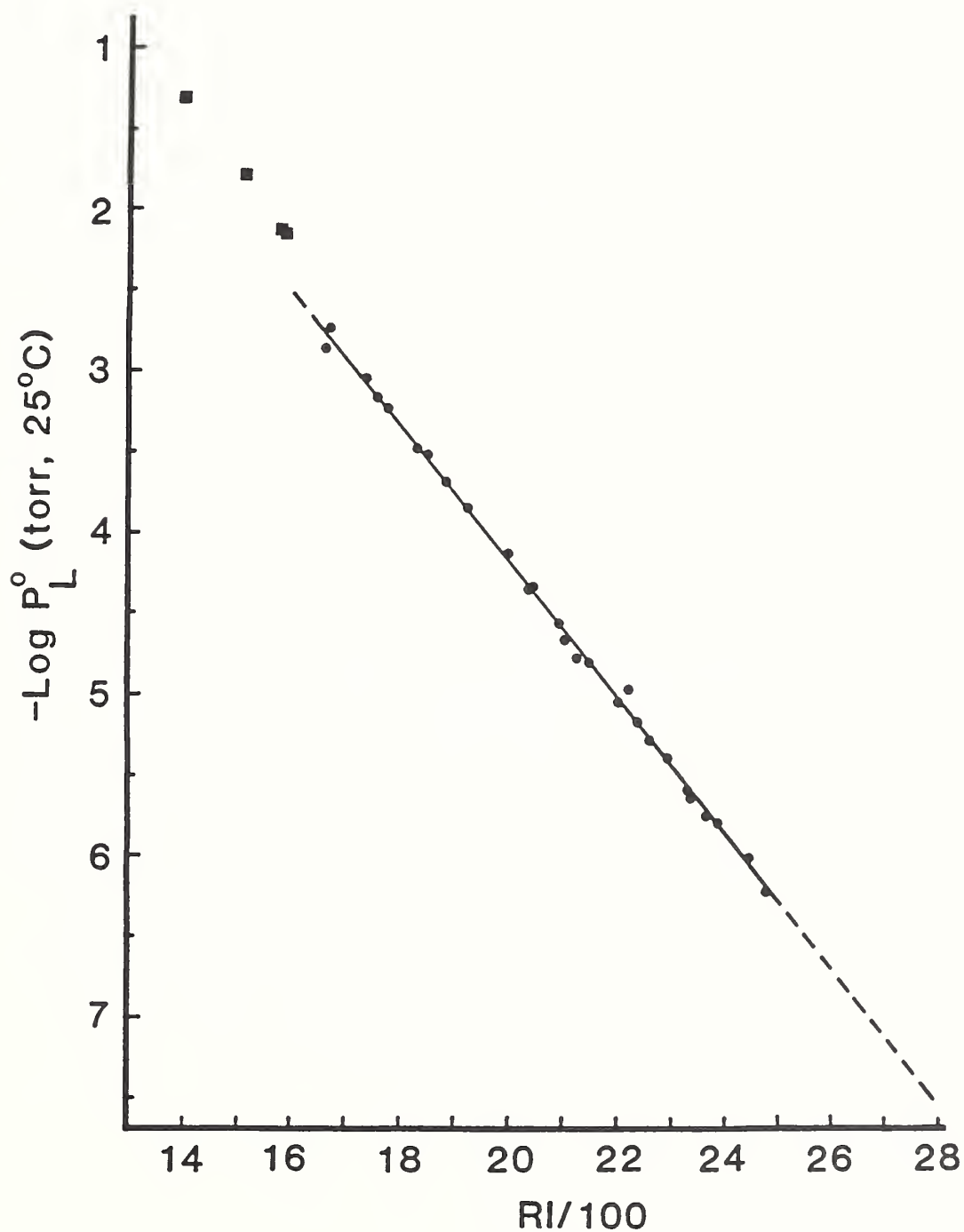


Fig. 2. Plot of $-\log P_L^0$ (torr, 25°C) vs. retention index at 200°C on OV-101 liquid phase. The 95% confidence interval is much smaller than in Fig. 1 (Table II) and is not shown. (■ and ● same as Fig. 1).



VAPOR-PARTICLE PARTITIONING OF SEMIVOLATILE ORGANIC
COMPOUNDS: ESTIMATES FROM FIELD COLLECTIONS

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ABSTRACT

Pesticides, polychlorinated biphenyls (PCB), and other semivolatile organic compounds (SOC) exist in air as vapors and associated with particulate matter. Factors influencing the vapor-to-particle distribution can be obtained from high volume sampling experiments using a glass fiber filter to collect particles and an adsorbent trap to collect vapors. Measurements of airborne organochlorine pesticides and PCB in four cities over a wide temperature range were used to estimate apparent partition coefficients $A(TSP)/F$, where A and F are the adsorbent- and filter-retained SOC concentrations (ng/m^3) and TSP is the total suspended particle concentration ($\mu\text{g}/\text{m}^3$). $A(TSP)/F$ were related to the average sampling temperature (T, Kelvin) through: $\text{Log } A(TSP)/F = m/T + b$. Fitted $\text{Log } A(TSP)/F$ at 20°C were closely correlated with $\text{Log } p_L^\circ$, the subcooled liquid vapor pressure. Heats of adsorption (ΔH_A), calculated from slopes m were at most 2-4 kcal/mol greater than subcooled liquid heats of vaporization ($\Delta H_{V,L}$), and in most cases indistinguishable from $\Delta H_{V,L}$ at the 95% confidence level.

INTRODUCTION

Semivolatile organic compounds (SOC) such as polychlorinated biphenyls (PCB), pesticides, heavy alkanes, and polycyclic aromatic hydrocarbons (PAH) exist in the atmosphere as vapors and associated with suspended particulate matter. The vapor-to-particle ratio (V/P) has an important influence on atmospheric removal by rain and dry deposition. Vapor scavenging is governed by the Henry's Law constant, the ratio of vapor pressure to water solubility. Some lower molecular weight SOC are rained out by vapor dissolution in raindrops; examples include phenols (1), 2-4 ring PAH (2-4), and hexachlorocyclohexane (HCH) (2-6). Other SOC which have substantial fractions in the particle phase and/or Henry's Law constants unfavorable for vapor scavenging are washed out of the atmosphere mainly on particles. Some compounds in the latter category are PCB and DDT (7,8), PAH of five or more rings (4), and n-alkanes (4). In the case of PCB and DDT, field-measured scavenging ratios greatly exceed those calculated from washout of the vapor phase (7). Within the suite of PCB congeners, those which are less volatile and have greater fractions on particles are preferentially deposited by rain and dry deposition (7,8).

Direct determination of V/P in ambient air is an experimentally challenging problem that has not yet been fully solved. SOC levels in ambient air are low, on the order of picograms to nanograms per cubic meter, and several hundreds or even thousands of cubic meters of air are usually sampled to provide enough material for analysis. A common high-volume (hi-vol) sampling technique is to pull air through a glass or quartz fiber filter (F) which retains particles followed by a solid adsorbent trap (A) to collect vapors. Frequently used adsorbents are polyurethane foam (PUF), Tenax-GC, XAD-2, and Florisil (9). The operational V/P is the ratio of the adsorbent-retained/filter-retained concentrations (A/F), both expressed in ng/m³.

How closely A/F represents V/P is uncertain. A/F may overestimate V/P because of the "blow-off effect" -- stripping of SOC from particles on the filter by the flowing airstream. It is also possible for the particle mass on the filter to act as an adsorbent, leading to an underestimation of V/P . Field collections using different sampling times and different types of filters have provided evidence for both processes, although blow-off losses are more commonly reported (10-15). A limitation of field measurements is that aerial concentrations and temperatures change during the normal sampling period of 24 h or longer, and whether blow-off losses or adsorption gains are observed will depend on how and when these variables change during a sampling period. For example, what is deposited on the filter at night may be desorbed again in the heat of the next day. The situation with PAH is complicated by the fact that degradative losses may also occur (16-21).

Despite these problems, A/F provides some insight to the factors influencing SOC vapor adsorption to atmospheric particulate matter. Knowing the relationship of A/F to sampling variables is also useful from an analytical standpoint. Here we present field A/F determinations for PCB and organochlorine pesticides in four cities. We have also carried out experiments in which particle-loaded filters were equilibrated with SOC vapors in the laboratory (22).

EXPERIMENTAL

Hi-vol samples were taken in four cities using a glass fiber filter backed up by an adsorbent cartridge. The cities were: Columbia, SC (1977-82); Denver, CO (January, 1980); a landfill at New Bedford, MA (June, 1980); and Stockholm, Sweden (1983-85). In most cases the adsorbent was PUF, and occasionally Tenax-GC and XAD-2 were used. Sampling times and air volumes were usually 24-48 h and 600-1200 m³.

Filters were desiccated overnight over anhydrous calcium sulfate (Drierite) and weighed to determine the particle load. PCB and organochlorine pesticides were solvent extracted from the filters and adsorbent cartridges, and determined by gas chromatography with electron capture detection. Samples from 1980 and earlier were quantified from packed column chromatograms, although some capillary GC was done for qualitative confirmation. Later samples (Columbia, 1982; and Stockholm, 1983-85) were quantified from capillary chromatograms.

The experiments in U.S. cities were also done to evaluate adsorbent collection efficiencies for PCB and pesticide vapors. The intent of the Stockholm study was to compare pesticide concentrations over northern Europe with those over North America and the North Atlantic. Details of collection and analytical methods are given in reports describing these projects (23-25).

RESULTS AND DISCUSSION

A summary of organochlorine and total suspended particle (TSP) concentrations in the four cities is given in Table I. Information for individual sampling days can be found in (23-25). Average levels of hexachlorobenzene (HCB) and hexachlorocyclohexane (HCH) among the cities were similar, whereas marked differences occurred for other organochlorines, notably PCB, DDT compounds, and chlordane. PCB concentrations in Stockholm air were unusually low compared to those in other cities (25). All of the Stockholm samples were taken in the winter, often when the ground was covered with snow, and these conditions may have retarded PCB evaporation from sources within the city.

Partitioning of organochlorines between the vapor phase and the particle mass on the filter was strongly influenced by volatility. A chromatogram of the PCB-containing fraction of a Stockholm air sample is shown in Figure 1. Higher proportions of the less volatile compounds can be seen on the filter compared to the

PUF trap, and even within the Aroclor 1254 pattern the heavier components are enriched on the filter. Other investigations of many SOC classes (PAH, phthalate esters, n-alkanes, fatty acids, and organochlorines) have shown that A/F decrease with increasing molecular weight and are lower for samples collected in winter compared to summer (4,7,14,15,26-30).

Yamasaki *et al.* (30) were the first to quantitatively express field A/F as a function of temperature and particle concentration. Samples were taken over 24-h periods for a year in Tokyo using a glass fiber filter followed by a PUF trap. A/F of individual PAH were related to average sampling temperature (T, Kelvin) and the TSP concentration by:

$$\text{Log } A(\text{TSP})/F = m/T + b \quad \text{Equation 1}$$

Regression fits to Equation 1 gave $r^2 \geq 0.8$ for most PAH. The Tokyo samples are the best field data on the adsorption of PAH to ambient air particulate matter.

Temperatures were fairly constant, varying by only 2.2-5.5°C over each collection period, so non-equilibrium effects caused by changes in vapor pressure with temperature were minimized.

Keller and Bidleman (28) collected PAH in Columbia, SC under conditions where the diurnal temperature changes were much larger, on the order of 10-20°C. Nevertheless, A/F partitioning of fluoranthene (FLA) and pyrene (PY) followed Equation 1, and the parameters m and b were reasonably close to those of the Tokyo samples.

The organochlorine data in this study were expressed as apparent vapor-particle partition coefficients, A(TSP)/F, with TSP in $\mu\text{g}/\text{m}^3$. The units of A(TSP)/F were thus $\text{ng SOC}/\text{m}^3 \text{ air} \div \text{ng SOC}/\mu\text{g particles}$. Single samples were usually taken on a particular date. However on some dates in Columbia parallel PCB samples were taken using rectangular 20 x 25-cm filters and 10-cm diameter filters. Actual filtering areas of these were 410 and 59 cm^2 , respectively. Volume flow rates were



about the same through the two filters, being limited mainly by the adsorbent cartridge, but face velocities across the round filters were nearly seven times higher. Replicate determinations of $A(TSP)/F$ for Aroclor 1254 are given in Table II, and the data show no consistent differences that can be attributed to filter size.

Plots of Equation 1 were made for high molecular weight PCB (Aroclor 1254), *p,p'*-DDE, *p,p'*-DDT, chlordane (cis- + trans-chlordane + trans-nonachlor), alpha-HCH, and HCB (Figure 2). A/F of PCB were measured in all four cities, and data for *p,p'*-DDE, *p,p'*-DDT, and chlordane were obtained in Columbia, Denver, and Stockholm. Measurable quantities of alpha-HCH and HCB on filters occurred only at low temperatures, so all A/F data were from Denver and Stockholm winter samples. Regression parameters of the Equation 1 plots are given in Table III, along with the best-fit $A(TSP)/F$ values at 20° and 0°C. The r^2 in the 0.83-0.90 range for PCB, *p,p'*-DDE, *p,p'*-DDT, and chlordane compare well with the PAH r^2 of Yamasaki *et al.* (30). Lower r^2 were obtained for alpha-HCH and HCB because of the smaller number of data points and greater scatter. As mentioned above, filter-retained residues for these two compounds approached the detection limits except at the coldest temperatures.

Several factors may have contributed to the scatter in the Figure 2. Day-to-night temperature fluctuations and changes in the concentration of organochlorines in air over the collection periods may have caused blow-off losses or adsorption gains to particles on the filter during individual experiments. The influence of relative humidity (RH) on SOC adsorption to particles is unknown, and although not measured, RH probably varied substantially over the course of these experiments. Finally, these data were obtained from measurements in several cities over eight years and were influenced by local differences in particle size distribution, surface area, and content of carbonaceous material. Considering the large list of variables,

it is surprising that the correlations are as good as they are. Volatility thus stands out as the primary factor governing SOC partitioning to urban aerosols.

The distribution of SOC between the particle mass on the filter and the absorbent trap is useful from an analytical standpoint. Filter-retained percentages of organochlorines that might be expected at 20° and 0°C and a TSP concentration of 60 $\mu\text{g}/\text{m}^3$ are listed in Table IV. These were calculated from the fitted $A(\text{TSP})/F$ in Table III. At sub-zero temperatures, substantial proportions of the heavier organochlorines are associated with particulate matter, which may increase their deposition rates.

If the interaction between SOC vapors and atmospheric particulate matter is relatively weak physical adsorption, the heats of adsorption (ΔH_A) calculated from the slopes (m) of Equation 1 plots (Table III) should be close to the heats of vaporization ($\Delta H_{v,L}$) of the liquid-phase solute (22, 31). Liquid-phase vapor pressures (p_L°) and $\Delta H_{v,L}$ of several SOC are listed in Table V. Most of these were calculated from literature averages of solid-phase vapor pressures (p_s°) given in an appendix to (32) using:

$$\ln p_L^\circ/p_s^\circ = 6.8 (T_m - T)/T \quad \text{Equation 2}$$

where T_m and T are the melting point and ambient temperatures (Kelvin) and 6.8 is a constant related to the entropy of fusion (33). A capillary GC method (32) was used to determine p_L° for cis- and trans-chlordane and trans-nonachlor. Relative retention data were also used to estimate $\Delta H_{v,L}$ of the chlordanes and p,p'-DDE.

An overall Aroclor 1254 "vapor pressure" of 7.7×10^{-5} torr at 25°C has been estimated by extrapolating high temperature data from Monsanto Corp. (34,35). This vapor pressure is biased toward the high side by some minor but volatile components of the Aroclor mixture. Our estimate of 1.4×10^{-5} torr at 20°C was made by summing the partial pressures of those congeners that were actually included in

the Aroclor 1254 analysis, *i.e.* the components indicated in Figure 1. Partial pressure data were obtained from (36).

The ΔH_A of Aroclor 1254, p,p'-DDE, p,p'-DDT, and chlordane are close to their respective $\Delta H_{V,L}$, an observation also made by Yamasaki *et al.* (37) for PAH. The fitted ΔH_A are greater than $\Delta H_{V,L}$ by about 2-4 kcal/mol, but the uncertainties in ΔH_A are large enough that ΔH_A and $\Delta H_{V,L}$ are not statistically different at the 95% confidence level, except in the case of Aroclor 1254. Confidence intervals of ΔH_A for alpha-HCH and HCB are larger (Table III), due to the greater scatter and fewer data points in the Equation 1 plots (Figure 2). Even though ΔH_A appear to be lower than $\Delta H_{V,L}$ for these two compounds, the differences are not significant at the 95% level. Determination of small differences between ΔH_A and $\Delta H_{V,L}$ that may exist requires more precise data than are obtainable from the present type of field measurements.

Figure 3 shows a log-log plot of the best-fit $A(TSP)/F$ at 20°C (Table 3) vs. p_L° . Included on this figure are PAH data from Yamasaki *et al.* (30) and Keller and Bidleman (28). Since the uncertainties in the Equation 1 parameters for alpha-HCH and HCB were larger than for the other organochlorines, we have also extrapolated $A(TSP)/F$ at 20°C from data obtained at sub-zero temperatures (where filter-retained quantities were more easily measurable) using slope $m' = -\Delta H_{V,L}/2.3R$ instead of the fitted slope $m = -\Delta H_A/2.3R$. The bars for alpha-HCH and HCB in Figure 3 thus represent the range of $A(TSP)/F$ at 20°C obtained using two different slopes in Equation 1.

$A(TSP)/F$ of the organochlorines and PAH were closely correlated with p_L° , and laboratory equilibration experiments (22) also showed that A/F partitioning of SOC was better explained by p_L° than p_g° . However, different regression lines for organochlorines and PAH can be seen in Figure 3. At a given p_L° , the proportion of PAH on particulate matter was higher than for organochlorines. One possible explanation is that PAH are planar molecules and may be more strongly adsorbed

than most of the organochlorines, only one of which is flat (HCB). If this were the case, differences between ΔH_A and $\Delta H_{V,L}$ should be larger for PAH than organochlorines. For Aroclor 1254, p,p'-DDE, p,p'-DDT, and chlordane, fitted $\Delta H_A - \Delta H_{V,L}$ were 2-4 kcal/mol (Table III), about the same as those found by Yamasaki *et al.* (37) for PAH. Therefore strength of adsorption does not appear to account for the differences in Figure 3.

It is likely that urban air contains some non-exchangeable PAH, bound to highly active sites or trapped within the particles. This PAH would not be in equilibrium with its vapor phase in the atmosphere, but would be extracted with solvent during analysis and counted along with the exchangeable PAH. Evidence for non-exchangeable PAH was presented by Eiceman and Vandiver (38), who used GC experiments to investigate the equilibrium between PAH vapors and fly ash. Irreversible adsorption occurred at low PAH concentrations, but once a layer of PAH had become attached to the particles, additional PAH was adsorbed reversibly. The inclusion of non-exchangeable PAH in the analysis of filter-retained particles would change the intercept but not the slope of Equation 1 plots, and could account for the different behavior of PAH and organochlorines (Figure 3).

Many uncertainties remain in our knowledge of vapor-particle interactions in ambient air. A major question, unanswered by field or laboratory (22) experiments is: How closely does A/F represent the true V/P in the atmosphere? It seems likely that the process of collecting particles on a filter will alter their size and surface area distributions from the situation where the particles were floating freely in the atmosphere. It is thus important to stress that the A(TSP)/F partition coefficients are between vapors and urban air particulate matter on filters, not airborne particles.

CONCLUSIONS

Field experiments have shown that SOC volatility, expressed by p_L° , is the dominating factor governing adsorption to urban air particulate matter. Differences in urban aerosols from city-to-city seem to be of secondary importance. Despite the inability to control the critical variables of temperature and vapor concentration, field studies of PCB and organochlorine pesticide partitioning have provided estimates of $A(TSP)/F$ and ΔH_A . The value of field experiments could be enhanced if collection and analytical techniques were developed to reduce the necessary sampling time to a few hours. Recent reports of SOC determinations in ambient air using low air volumes show advances in this area (40,41).

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Table I. Average Organochlorine^a and TSP Levels in Four Cities

City	ng/m ³					µg/m ³	
	PCB	DDE	DDT	Chlordane	HCH	HCB	TSP
Columbia, SC	1.5	0.093	0.048	1.3	0.9	0.29	53
Denver, CO	0.45	0.021	0.043	0.063	0.22	0.24	175
New Bedford, MA (landfill)	9.3						193
Stockholm, Sweden	0.067	0.0034	0.0061	0.010	0.40	0.065	34

a) PCB = Aroclor 1254, DDE and DDT = p,p'-DDE and p,p'-DDT, Chlordane = cis- + trans-chlordane + trans-nonachlor, HCH = alpha-hexachlorocyclohexane, HCB = hexachlorobenzene

Table II. Replicate Determinations of A(TSP)/F for Aroclor 1254

Collection Dates ^a Median Temp. Air Volume	Filter Type ^b	ng /m ³		µg/m ³ TSP	Log A(TSP)/F
A	F				
Dec. 18-19, 1977 10°C 300m ³	A	0.71	0.062	59 ^c	2.830
	A	0.92	0.047		3.063
	A	1.3	0.081		2.976
Mar. 16-17, 1979 9°C 720m ³	A	0.72	0.031	58 ^c	3.129
	A	0.85	0.030		3.216
Apr. 3-5, 1980 18°C 1280m ³	A	0.68	0.031	48 ^c	3.022
	B	0.80	0.020		3.283
Oct. 16-17, 1980 20°C 650m ³	A	0.99	0.040	68	3.226
	A	1.3	0.032	63	3.408
	A	1.3	0.042	57	3.247
	B	1.8	0.035	51	3.419
	B	1.4	0.034	53	3.339

a) All samples from Columbia, SC

b) A = 20x25-cm B = 10-cm diameter

c) One filter weighed for TSP determination.

Table III. Equation 1 Regression Parameters for Organochlorines

	m	b	r ²	n	Log A(TSP)/F ^a		$\Delta H_a \pm 95\% \text{C.I.}$
					0°C	20°C	
alpha-HCH	-2755	14.286	0.574	11	4.194	4.883	12.6 ± 8.2
HCB	-3328	16.117	0.687	8	3.925	4.758	15.2 ± 10.3
Aroclor 1254	-4686	19.428	0.885	34	2.265	3.436	21.4 ± 2.7
Chlordane	-4995	21.010	0.901	18	2.711	3.960	22.9 ± 4.0
p,p'-DDE	-5114	21.048	0.881	15	2.320	3.598	23.5 ± 5.2
p,p'-DDT	-5870	22.824	0.885	18	1.320	2.788	26.9 ± 5.1

a) Units of A(TSP)F are ng SOC/m³ air ÷ ng SOC/μg particles.

Table IV. Average Percent Filter-Retained Organochlorines at
TSP = 60 $\mu\text{g}/\text{m}^3$

	20°C	0°C
alpha-HCH	0.08	0.4
HCB	0.1	0.7
Chlordane	0.7	11
p,p'-DDE	2.0	24
Aroclor 1254	2.1	25
p,p'-DDT	8.9	74

Table V. Vapor Pressures and Heats of Vaporization^a of Organochlorines and PAH

	p°_L , torr (20°C)	$\Delta H_{V,L}$ kcal/mol
Organochlorines		
alpha-HCH	6.3×10^{-4}	16.4
HCB	1.4×10^{-3}	17.4
Aroclor 1254	1.4×10^{-5}	17.0
trans-chlordane	2.9×10^{-5}	19.9
cis-chlordane	2.2×10^{-5}	20.2
trans-nonachlor	1.7×10^{-5}	20.4
p,p'-DDE	1.3×10^{-5}	21.2
p,p'-DDT	1.3×10^{-6}	23.3
PAH		
phenanthrene	6.2×10^{-4}	17.2
anthracene	4.1×10^{-4}	16.5
fluoranthene	4.2×10^{-5}	15.1
pyrene	7.3×10^{-5}	18.1
benzo(k)fluoranthene	3.7×10^{-8}	24.4
benzo(e)pyrene	9.6×10^{-8}	22.4
benzo(a)pyrene	9.2×10^{-8}	22.2

$\Delta H_{V,L}$ were calculated from slopes of $\text{Log } p^{\circ}_L$ vs $1/T$ plots (p°_L obtained from p°_S using Equation 2) for alpha-HCH, HCB, p,p'-DDT, and PAH. Aroclor 1254 $\Delta H_{V,L}$ calculated from Monsanto Corp. data (35). $\Delta H_{V,L}$ for the chlordanes and p,p'-DDE were derived from gas chromatographic retention data (36).

FIGURES

1. PCB, p,p'-DDE, and HCB in an air sample from Stockholm, January, 1985.
Most organochlorine pesticides have been removed by silicic acid fractionation. Column: 25-m BP-1 bonded phase (SGE Corp.).
2. Equation 1 plots for organochlorines:
 - Columbia, SC
 - New Bedford, MA
 - ▲ Denver, CO
 - ◆ Stockholm, Sweden
3. Relationships between $A(TSP)/F$ at 20°C and p_L° . Circles and bars = organochlorines. HCB = hexachlorobenzene, HCH = alpha-hexachlorocyclohexane, CHLOR = cis + trans-chlordane + trans-nonachlor, A. 1254 = Aroclor 1254, DDE and DDT = p,p'-DDE and p,p'-DDT. Bars for HCH and HCB span the range of $A(TSP)/F$ at 20°C obtained by extrapolating Equation 1 with regression slopes m (Table III) or slopes $m' = -\Delta H_{v,L}/2.3R$. Filled triangles = PAH in Tokyo, ref. (30); open triangles = PAH in Columbia, ref. (28). PH = phenanthrene, FLA = fluoranthene, PY = pyrene, BkF = benzo(k)fluoranthene, BaP and BeP = benzo(a)- and benzo(e)pyrene.



STOCKHOLM AIR

AROCLOR 1254

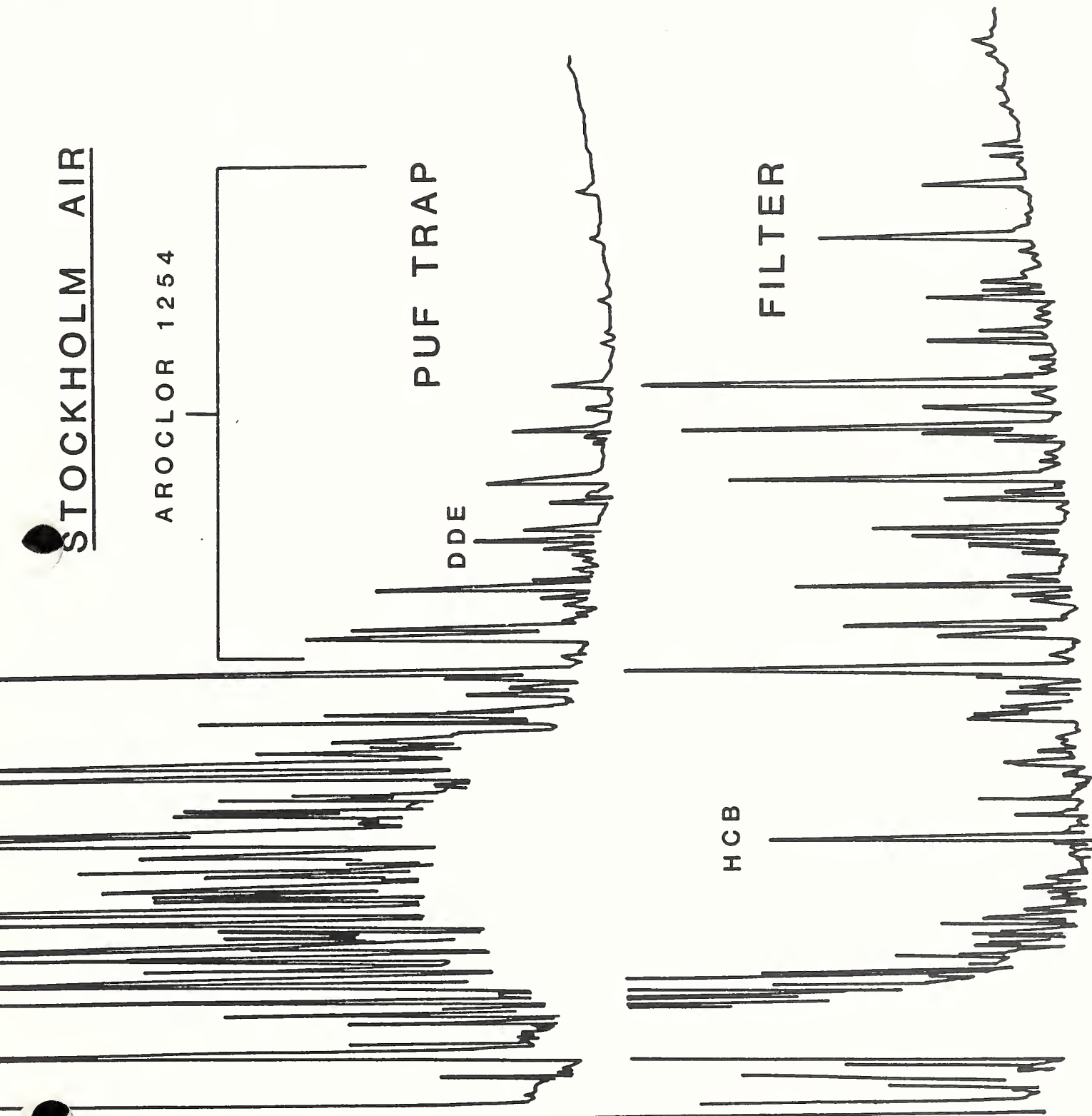
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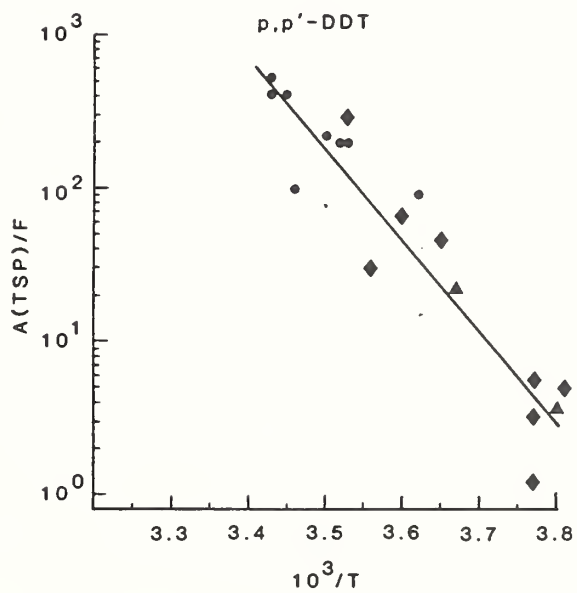
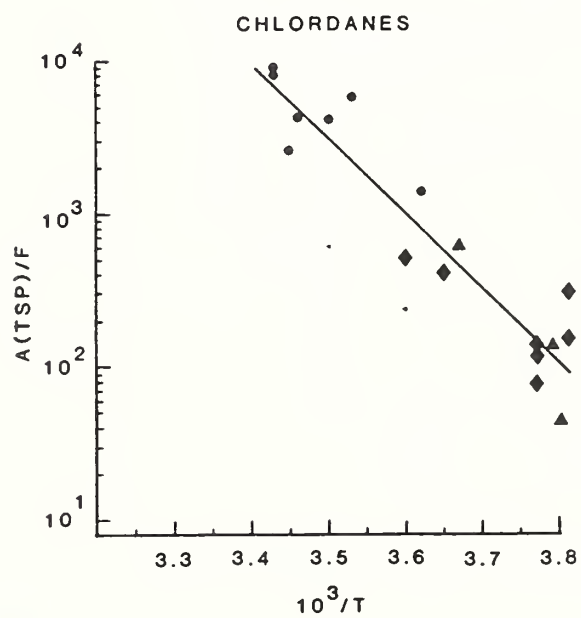
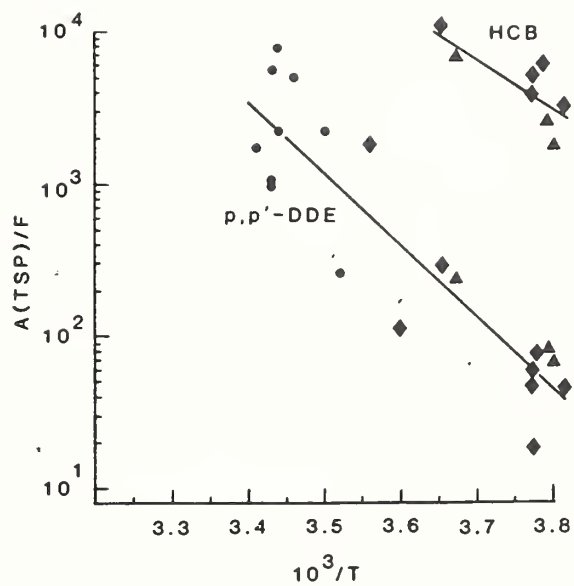
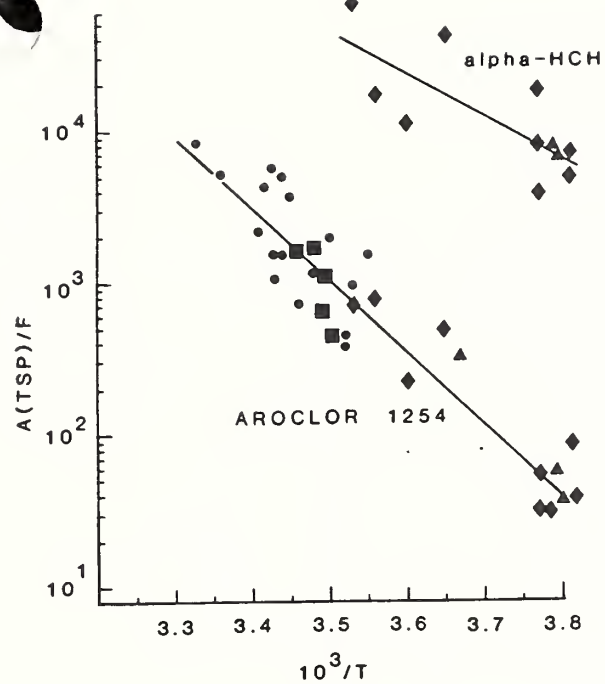
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FILTER

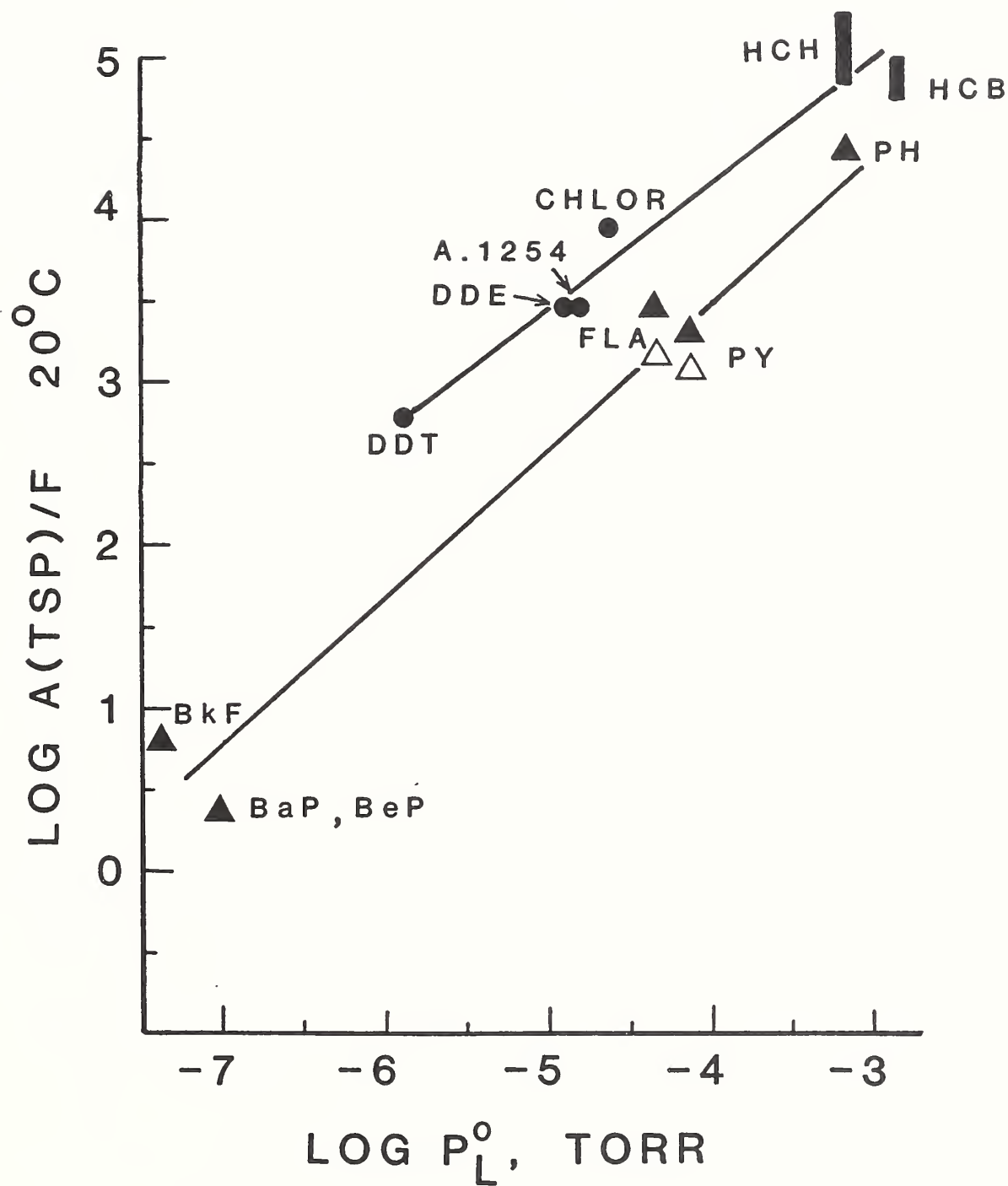
HCB

F-1





F.3



An Experimental System for Investigating Vapor-Particle
Partitioning of Trace Organic Pollutants

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ABSTRACT

An apparatus was designed to equilibrate urban air particulate matter on a filter with controlled vapor concentrations of semivolatile organic compounds (SOC) at 20°C under simulated air sampling conditions. Vapor-particle distributions (V/P) for organochlorine pesticides and 3-4 ring polycyclic aromatic hydrocarbons were estimated from laboratory measurements of the apparent partition coefficient $A(TSP)/F$, where A and F are the adsorbent- and filter-retained SOC concentrations (ng/m^3) and TSP is the total suspended particle concentration ($\mu\text{g}/\text{m}^3$). Laboratory measured $A(TSP)/F$ correlated well with the subcooled liquid phase vapor pressures (p_L^0) of the SOC tested, but not with their solid phase vapor pressures. Comparisons of field and laboratory $A(TSP)/F$ were made and implications of p_L^0 -dependent partitioning to the atmospheric chemistry of SOC are discussed.

INTRODUCTION

Semi-volatile organic compounds (SOC), including 3-4 ring polycyclic aromatic hydrocarbons (PAH), pesticides, polychlorinated biphenyls (PCB), dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF), exist in ambient air as vapors and attached to suspended particles. Knowledge of SOC vapor/particle distribution (V/P) is fundamental to understanding the atmospheric transport of these pollutants, because V/P influences the method by which the contaminant returns to the earth and the atmospheric residence time. V/P is also an important consideration in developing sampling methods and designing pollution control systems.

Factors influencing V/P in ambient air can be obtained using conventional high volume (hi-vol) sampling. Air is pulled through a glass fiber filter (F) to collect particles, and then through an adsorbent trap (A) to collect the vapors. Operationally, the apparent V/P is estimated by the adsorbent-to-filter retained ratio (A/F). In previous investigations, A/F for organochlorines (OC) (1) and PAH (2,3) were determined from hi-vol field experiments in several cities. Results of these studies revealed that A/F was related to the average sampling temperature (T, Kelvin) and the total suspended particle concentration (TSP, $\mu\text{g}/\text{m}^3$) by:

$$\text{Log } A(\text{TSP})/F = m/T + b \quad (\text{Equation 1})$$

where A is the adsorbent-retained SOC and F is the filter-retained SOC, both in ng/m^3 . $A(\text{TSP})/F$ has units of

ng SOC/m³ air ÷ ng SOC/μg particles, = C_A/C_P.

The strong dependence of A/F on temperature suggested a general relationship based on SOC volatility. Plots of field A(TSP)/F at 20°C versus OC and PAH vapor pressures revealed that A/F partitioning is controlled largely by the subcooled liquid vapor pressure (p_L⁰) and not the solid phase vapor pressure (p_S⁰) (1,4).

How closely A/F represents the true V/P in the atmosphere remains uncertain. Sampling times of 12 h or more are usually necessary to collect enough SOC for analysis. During the collection period SOC concentrations and especially ambient temperatures are likely to change, resulting in blow-off losses from or adsorption gains to the particle load on the filter (4,5-10). Other factors which may affect A/F are variations in particulate matter including size distribution, surface area, and content of carbonaceous material. The influence of relative humidity on A/F is also unknown. Additional considerations include the possibility of degradative losses, for example in reactions of PAH with O₃ and NO_x (11-16).

In this article we describe a laboratory equilibration system for investigating the adsorption of OC and PAH vapors to particle-loaded filters under controlled temperature and vapor concentration conditions. The apparatus was designed and constructed to closely simulate a hi-vol field sampler.

EXPERIMENTAL

Field Collection and Analysis of Particles

Particle-loaded filters used in laboratory

equilibration experiments were obtained by pulling air at approximately 1.0 m³ min⁻¹ for 45-76 h through a 20 x 25-cm type A/E glass fiber filter (Gelman Sciences, Ann Arbor, MI) using conventional hi-vol TSP collectors (General Metal Works Inc., Village of Cleves, OH) (17). Filters were precleaned by wrapping in solvent-rinsed aluminum foil and baking at 425°C for 6 h. Three sets of particle-loaded filters were collected on the roof of a two-story building in Columbia used by the South Carolina Department of Health and Environmental Control as a TSP monitoring site. Four or five particle-loaded filters were obtained on each sampling date, one of which was used for total carbon (TC) and total nitrogen (TN) analyses. An additional sampler containing a filter backed with three 7.8-cm diameter x 7.6-cm thick polyurethane foam (PUF) plugs (density = 0.022 g cm⁻³) provided both particle and vapor-phase SOC collection. Details for preparing and precleaning PUF plugs and collecting field samples have been published elsewhere (2,18-21).

Before and after sampling, filters were desiccated overnight over anhydrous calcium sulfate (Drierite) and weighed to obtain TSP. TC and TN were determined on 2-cm diameter disks cut from 4-6 sections of a particle-loaded filter using a cork borer. Each disk was finely ground with an agate mortar and pestle. The ground material (19-24 mg) was weighed into an aluminum boat using a Sartorius Model 4530 microanalytical balance. Oxidizing catalyst (Type 185, Hewlett-Packard Co., Avondale, PA) was added to each boat

and the samples were combusted in a Hewlett-Packard Model 185B CHN Analyzer using standard operating conditions (22). NBS standard cystine 143B (29.99% C, 11.66% N) was used to prepare a calibration curve. Combustion of 0.12-0.24 mg activated carbon gave $84 \pm 1\%$ recovery. Blanks were analyzed to correct for TC and TN in the filter matrix. Analytical procedures for extraction, cleanup, fraction, and quantification of PAH and OC on filters and PUF plugs are detailed below.

Vapor-Particle Equilibration Experiments

The apparatus to equilibrate particle-loaded filters with SOC vapors (V-P experiments) is shown in Figure 1. A prefilter assembly to provide particle- and SOC-free laboratory air was composed of a glass fiber filter in a 20 x 25-cm hi-vol filter holder followed by an 8.3-cm diameter x 3-cm thick bed of activated carbon (Fisher Scientific, 6-14 mesh, resieved, precleaned by soxhlet extraction with acetone and dichloromethane, and vacuum-dried at 40°C) sandwiched between two 1.5-cm thick PUF plugs. The prefilter was followed by a 12.5 x 15.0 x 100-cm stainless steel mixing chamber where SOC vapors were introduced using generator columns, and then by two 20 x 25-cm filter holders attached face-to-face and containing the particle-loaded and back-up clean filters. SOC vapor concentrations behind the filters were monitored by two 7.8-cm diameter x 7.6-cm thick PUF plugs in an aluminum canister, which was attached by 5 m flexible hose to a Rotron DR-313 brushless pump (Rotron Corporation, Woodstock, NY). The apparatus was located in a

room thermostated at $20 \pm 1^{\circ}\text{C}$, and the pump exhaust was vented to the outside. All seals were made using solvent-rinsed silicone rubber gaskets (Niantic Rubber, Cranston, RI). Flow rates were related to the pressure drop behind the sampling train using an orifice calibrator. Measurements of pressure drop in the system in front of and immediately following the loaded filter holder indicated reductions of 0.040 atm and 0.063 atm respectively.

Generator columns to produce SOC vapors are shown in Figure 2. The columns were prepared by packing precleaned glass beads (2 mm diameter) or sand (6-14 mesh, washed with 12M HCl, deionized water, and baked at 1000°C for 6 h) into a solvent-rinsed 5- or 10-mL plastic syringe barrel. Approximately 50-75 mg test compound in dichloromethane was added, and the column was allowed to stand uncapped overnight in a hood to ensure complete evaporation of the solvent. Silanized glass wool was placed on top of the support and the column was capped with either a rubber serum cap (most volatile compounds), one-holed size #0 rubber stopper (column flows of 7-20 mL/min), or plug of PUF (least volatile compounds, column flows >20mL/min) depending on the flow rate (vapor concentration) requirements. Syringe needles (16-27 gauge) pushed through the serum cap provided a method of varying flow rates (2-7 mL/min) through generator columns containing the more volatile SOC. The Luer lock end of the generator column was fitted with an Acrodisc CR 0.2 μm filter (Gelman Sciences), and the tapered end of the Acrodisc was connected to the mixing chamber of

the equilibration apparatus using a rubber stopper. Before beginning the V-P experiments, the generator columns were preconditioned by running the apparatus for 3-4 h without the test filters in place.

Test compounds were phenanthrene (PH), anthracene (AN), fluoranthene (FLA), and pyrene (PY), obtained from the Foxboro Company, New Haven, CT; and hexachlorobenzene (HCB), alpha- and gamma-hexachlorocyclohexane (α -HCH and γ -HCH), cis- and trans-chlordane (c-CHLOR and t-CHLOR), 2,2-bis(2-chlorophenyl)-1,1-dichloroethene (p,p'-DDE), and 2,2-bis(2-chlorophenyl)-1,1,1-trichloroethane (p,p'-DDT), obtained from the EPA Pesticide and Industrial Chemicals Repository, Research Triangle Park, NC.

V-P experiments were conducted by exposing two 20 x 25-cm filters to vapors of test compounds at $20^{\circ} \pm 1^{\circ}\text{C}$ for varying times and air volumes. The front filter was loaded with approximately 100-250 mg urban air particulate matter collected in Columbia as described above. The back filter was a blank to correct for adsorption to the filter matrix. The first plug in the PUF trap behind the filters was changed every 2-3 h and analyzed to determine changes in vapor concentration with time. The back-up plug acted as a procedural blank, except for HCB and α -HCH which were volatile enough to exhibit slight breakthrough from the first plug ($\leq 2\%$ of the total vapor phase material collected during a run.)

Analytical Methods

Filters were cut into strips and refluxed for 24 h in dichloromethane. PUF plugs were soxhlet extracted for 24 h in petroleum ether. Extracts were reduced to 5 mL on a rotary evaporator, and filter extracts were transferred to hexane during this step. For V-P experiments involving only OC, column chromatography cleanup and fractionation was not necessary, and filter and plug extracts were analyzed at this point by electron capture gas chromatography (GC-ECD) as described below.

Field samples and V-P experiment filter samples involving PAH were cleaned and fractionated using an alumina-silicic acid column chromatography procedure previously described (2), except that the column was eluted with 25 mL petroleum ether (fraction 1) and then 20 mL 30% dichloromethane-petroleum ether (fraction 2). Fraction 1 contained PCB, HCB, and p,p'-DDE; fraction 2 contained PAH, HCH, p,p'-DDT, cis- and trans-chlordane, trans-nonachlor, and toxaphene components. Fractions were reduced to 2 mL using a gentle stream of N₂ and transferred to 10 mL centrifuge tubes. Fraction 2 eluates were transferred to hexane during this step. Sample volumes were then adjusted for quantitative analysis using a stream of N₂.

PAH in fraction 2 were analyzed using high performance liquid chromatography (HPLC) with fluorescence detection. The HPLC system was the same as that previously described (2), except that the compounds were separated on a 25 cm x 4.6 mm i.d. Vydac 201TP104 10 μm reversed phase C-18 column

(The Separations Group, Hesperia, CA), preceded by a MPLC NewGuard column containing an RP-18 cartridge (Brownlee Labs, Santa Clara, CA). Field samples analyzed for 3-5 ring PAH were run using the solvent program: initial 55% CH₃CN-H₂O, increasing at 2.4% CH₃CN min⁻¹ to a final 95% CH₃CN-H₂O mixture. V-P experiment samples were analyzed only for PH, AN, FL, and PY using a 65% CH₃CN-H₂O isocratic mobile phase.

OC were determined by GC-ECD after shaking extracts with concentrated H₂SO₄ to remove interfering compounds. Analyses were carried out on a Varian 3700 instrument using splitless injection (1-2 μ L, 30 seconds), with the column held at 90°C for 1 min and then increased at 5°C/min to 275°C. Either a 12 m or a 25 m x 0.22 mm i.d. BP-5 column (SGE Inc., Austin, TX) with a 0.25 μ m film thickness was used. Other analysis conditions were: H₂ carrier gas 2 mL/min, split flow 80 mL/min, injector and detector temperatures 220°C and 320°C, respectively. Chromatographic data were collected using a Hewlett-Packard 3390A or a Shimadzu Chromatopac C-R3A integrator. PAH and OC were quantified from peak area and height, respectively.

RESULTS AND DISCUSSION

Table I summarizes the collection and filter analytical data and SOC aerial concentrations for the three field collection periods. Concentrations of TSP, TC, OC, and PAH were comparable to those previously reported for Columbia (2,20,21,23). Although present, HCB, α -HCH, PH and AN are not reported, since these compounds were not quantitatively collected on PUF at the high air volumes.

Ten V-P experiments were conducted over the range of vapor concentrations and equilibration times (air volumes) in Table II. Up to eight compounds could be tested during a single run. No γ -HCH generator column was used for 4 of the 7 runs, even though this compound was detected in the vapor phase and on the particle-loaded filter for these experiments. Subsequent analysis of material in the α -HCH generator column revealed that the γ -isomer was present at 0.3% of the α -HCH, so the low levels of γ -HCH in these experiments probably arose from this source.

Figure 3 depicts changes in vapor concentration (C_A) behind the exposed filters with air volume (time). The PAH curves represent one run totaling 587 m³ air (about 22 h) and the OC a different experiment totaling 770 m³ (30 h), with each point representing 3 h intervals. Concentrations of the more volatile compounds stabilized quickly and remained reasonably constant over the entire run. A lag time of about 3-9 h was observed before the less volatile compounds reached stable levels. In these cases, C_A was obtained using the final points in the plateau region; e.g., the mean of the last four p,p'-DDT points in Figure 3. The rapid attainment of steady state by the more volatile compounds suggests that the lag time observed for the heavier SOC was due to their adsorption by the particles on the filter.

SOC residues on back-up filters averaged 10% or less of those on the particle-loaded filters (Table II), and an exposure experiment conducted with two clean filters in the

01 V-P apparatus revealed that SOC were being adsorbed by the filter matrix itself. However, these experiments could not rule out the possibility that a portion of SOC found on the backup filter was due to migration of very small particles from the particle-loaded filter. Backup filter residues were subtracted from those on the front filter to provide the mass of SOC on particles.

Figure 4 is a plot of C_P versus C_A for three OC. The partition coefficient C_A/C_P was constant over two orders of magnitude change in C_A , indicating that the V-P experiments were conducted within the linear region of the adsorption isotherm ($r^2 = 0.995, 0.984, \text{ and } 0.964$ for γ -HCH, p,p'-DDE and p,p'-DDT, respectively).

$A(\text{TSP})/F (= C_A/C_P)$ from V-P experiments are summarized in Table III and Figures 5 and 6. The linearity of the adsorption isotherms (Figure 4) and the constancy of $A(\text{TSP})/F$ with air volume (Figures 5 and 6) are rather remarkable, considering that three different lots of urban air particulate matter were used for the experiments. Field studies of OC and PAH partitioning at various urban sites have likewise indicated that the particulate matter source is less important than other factors (1-3).

Saturation vapor pressures of the crystalline solid (p_S^O) and subcooled liquid (p_L^O) PAH and OC are given in Table IV. The vapor pressures can be interconverted through:

$$\ln p_L^O/p_S^O = 6.8(T_m - T)/T \quad (\text{Equation 3})$$

where T_m and T are the melting point and ambient

temperatures (Kelvin) and 6.8 is a constant related to the entropy of fusion (24). Differences between p_S^O and p_L^O increase rapidly with melting point. At 20°C p,p'-DDE (mp 89°C) has a p_L^O five times higher than p_S^O , whereas the difference is a factor of 130 for HCB (mp 230°C) (Table IV).

Figure 7 shows a log-log plot of the average laboratory $A(TSP)/F$ for OC at 20°C (Table III) vs. p_S^O . This plot shows a good deal of scatter ($r^2 = 0.800$), especially for the higher melting compounds α -HCH and HCB (Table IV). A similar plot vs. p_L^O (Figure 8) gave an excellent correlation ($r^2 = 0.998$). $A(TSP)/F$ from hi-vol collections in several cities were also well correlated with p_L^O (1,25). The vapor pressure over a solid is reduced relative to its subcooled liquid because of the crystal lattice energy. When individual solute molecules condense on an indifferent surface (i.e., physical adsorption), no solute crystal lattice is present and the adsorption might be expected to be controlled by p_L^O rather than p_S^O . Several lines of evidence indicate that some environmentally important phase distributions are controlled by liquid-phase physical properties: Yamasaki et al. (25) found that the heats of adsorption (ΔH_A) of PAH onto urban air particulate matter were close to the subcooled liquid PAH heats of vaporization ($\Delta H_{V,L}$). We observed similar behavior for OC (1). Breakthrough of PAH and OC vapors on solid adsorbent collection traps is governed by p_L^O rather than p_S^O (26,27). Bioconcentration factors and octanol-water partition coefficients are inversely related to the water solubility

of the subcooled liquid phase (28). Figure 8, along with field data (1), strongly supports p_L^0 as the relevant property for describing A/F partitioning of non-polar OC.

A(TSP)/F for the four PAH in relation to the OC are also shown in Figure 8. The PAH correlation to p_L^0 ($r^2 = 0.904$) is not as close as in the case of the OC ($r^2 = 0.998$), though it is much better than the correlation with p_S^0 ($r^2 = 0.445$). The PAH also exhibit a somewhat greater affinity for the particle-loaded filter than do the OC. One explanation is that PAH are planar molecules, and may be adsorbed more strongly than most of the OC, only one of which is flat (HCB). As pointed out in our earlier article (1), differences between ΔH_A and $\Delta H_{V,L}$ should be larger for PAH than OC to support this hypothesis. However, field results indicate that fitted $\Delta H_A - \Delta H_{V,L}$ for OC (1) were about the same as those for PAH (25). An alternate explanation is that urban air particulate matter contains some non-exchangeable PAH. These PAH molecules may be bound to highly active sites on the particle surface, or they may have become trapped within the particle matrix. This bound material would be unavailable for V-P partitioning, but would be extracted with solvent during analysis and counted along with the exchangeable fraction. Eiceman and Vandiver (29) presented evidence for non-exchangeable PAH adsorption to fly ash at low vapor concentrations.

A(TSP)/F from field (1) and laboratory experiments with OC are compared in Table III and Figure 9. Also included in this plot is a field value for higher molecular weight PCB

(Aroclor 1254), with an estimated vapor pressure of 1.4×10^{-5} torr at 20° (1). The field and laboratory agreement is good for the chlordanes, p,p'-DDE, and p,p'-DDT, and the field Aroclor 1254 point is also close to the laboratory line. However the agreement is less satisfactory for α -HCH and HCB. As mentioned previously (1), filter-retained quantities of these two volatile OC in field samples were difficult to determine except at cold temperatures, and the uncertainties in extrapolating Equation 1 plots to 20° were large. This may in part account for the field and laboratory differences seen in Figure 9. The agreement for α -HCH can be improved by assuming a slope for its Equation 1 plot equal to $m' = -\Delta H_{V,L}/2.3R$ (dashed circle in Figure 9) (1). However the situation of HCB is not greatly improved.

A comparison of field (triangles) (2,3) and laboratory (circles) $A(TSP)/F$ for the PAH are given in Table III and shown in Figure 10. The open triangles are field data from Columbia (2) and the solid triangles are the Tokyo field data of Yamasaki et al., (3). Yamasaki et al. were unable to separate PH and AN by GC, but since urban air contains an order of magnitude more PH than AN (2), the $A(TSP)/F$ was plotted against the p_L^0 of PH. As with HCB, the PAH field $A(TSP)/F$ fell below their laboratory values. An explanation for PAH and also HCB may lie in the different ways that SOC become bound to particles in urban air vs. in V-P experiments. Vapors introduced in the V-P experiments probably condensed on the surface of the particles on the filter. SOC on filters from the field collections also

included material trapped within the particle matrix or strongly adsorbed to active sites, i.e. non-exchangeable SOC. Differences between laboratory and field $A(TSP)/F$ might be expected to be greatest for SOC that become incorporated into the particles at the time of formation and less for SOC that condense onto the particles later in their lifetimes. SOC in the former category include combustion-derived compounds such as PAH and HCB (30), and it is for HCB that we found the greatest difference between laboratory and field $A(TSP)/F$. OC pesticides probably enter urban air as vapors via transport from agricultural land or by evaporation from treated areas within the city (e.g., chlordane, used in structural termite control) and then condense onto urban aerosols. For these compounds, laboratory and field $A(TSP)/F$ agree well.

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Table I. Filter Collection Data and Aerial Concentrations of
SOC in Columbia, SC.

	sampling date		
	Oct 30-Nov 1	April 2-5	Aug 26-28
	1984	1985	1985
m ³ air	1268 ^a , 2800 ^b	2006 ^a , 4850 ^b	1535 ^a , 3300 ^b
temperature (°C)			
median	20.6	18.3	25.5
range	18.9-29.4	5.0-28.3	22.2-31.7
TSP (μg/m ³)	46.6	49.8	59.4
total carbon (% of TSP)	16	19	12
total nitrogen (% of TSP)	2.6	2.0	1.6
<u>Organochlorines (A+F)^c</u>	<u>ng/m³</u>	<u>ng/m³</u>	<u>ng/m³</u>
γ-HCH	0.31	0.14	0.43
<u>trans</u> -chlordane	0.81	0.29	1.3
<u>cis</u> -chlordane	0.40	0.14	0.78
<u>trans</u> -nonachlor	0.31	0.11	0.50
p,p'-DDE	0.11	0.033	0.17
p,p'-DDT ^d	0.12	0.026	0.068
Aroclor 1016	0.55	0.74	1.7 ^e
Aroclor 1254	0.47	0.32	0.59
toxaphene	1.5	0.43	1.43

Table I (cont.)

<u>PAH (A+F)^c</u>	<u>ng/m³</u>	<u>ng/m³</u>	<u>ng/m³</u>
fluoranthene	4.9	7.2	12
pyrene	6.3	12	16
benzo(k)fluoranthene	---	0.10	0.078
benzo(a)pyrene	---	0.11	0.12
benzo(g,h,i)perylene + dibenz(a,h)anthracene	---	1.0	0.55
indeno(1,2,3-c,d)pyrene	---	0.54	0.33
coronene	---	0.84	0.51

^a Filter-PUF sampler used for SOC analysis.

^b Filter only samplers used for laboratory equilibration experiments.

^c HCB, α -HCH, phenanthrene, and anthracene were not quantitatively collected because of breakthrough losses on PUF.

^d Estimated concentration due to co-elution with toxaphene components.

^e PUF only.

^a Table II. Range of Conditions and Test Compounds on the Back-up Filter During Laboratory Vapor-Particle Equilibration Experiments.

compound	experiments	vapor concentration ng/m ³	air volume m ³	average % on back-up filter ^a
phenanthrene	6	445-574	153-1357	ND ^b
anthracene	5	22- 30	153-1357	ND ^b
fluoranthene	7	4.8- 45	153-1357	1.2± 1.1
pyrene	5	9.7- 22	153-1357	0.2± 0.5
hexachlorobenzene	7	30- 87	153-828	5.3± 5.1
α-HCH	7	53-160	229-794	6.5± 5.3
γ-HCH	7	1.0-252	153-794	7.4± 7.1
<u>trans</u> -chlordane	7	17- 56	229-794	10.6±10.3
<u>cis</u> -chlordane	8	8.7- 40	153-794	6.3± 6.7
p,p'-DDE	8	0.11- 27	153-1357	2.3± 2.3
p,p'-DDT	6	0.013-1.5	229-1357	6.9± 5.0

^a (ng on back-up filter ÷ ng on particle-coated filter) x 100.

^b Not detected. (Limits of detection were 7 ng PH and 1.5 ng AN.)

Table III. Comparison of A(TSP)/F from Laboratory Experiments and Field Studies.

compound	A(TSP)/F (20°C) ^a	
	laboratory ^b	field ^c
phenanthrene	$(9.4 \pm 1.1) \times 10^4$	--
anthracene	$(6.5 \pm 1.1) \times 10^4$	--
fluoranthene	$(5.0 \pm 1.5) \times 10^3$	$1.3 \times 10^3, 2.8 \times 10^3$
pyrene	$(2.8 \pm 0.7) \times 10^3$	$1.2 \times 10^3, 1.9 \times 10^3$
hexachlorobenzene	$(6.8 \pm 2.9) \times 10^5$	$5.7 \times 10^4, 9.7 \times 10^4$ d
α-HCH	$(2.3 \pm 0.4) \times 10^5$	$7.6 \times 10^4, 1.8 \times 10^5$ d
γ-HCH	$(8.1 \pm 1.6) \times 10^4$	--
<u>trans</u> -chlordane	$(1.1 \pm 0.2) \times 10^4$	9.1×10^3 e
<u>cis</u> -chlordane	$(1.0 \pm 0.1) \times 10^4$	
p,p'-DDE	$(4.5 \pm 1.2) \times 10^3$	4.0×10^3
p,p'-DDT	$(5.6 \pm 1.8) \times 10^2$	6.1×10^2

^a Units of A(TSP)/F are ng SOC/m³ air ÷ ng SOC/μg particles.

^b Average of laboratory experimental values.

^c Obtained from plots of Equation 1. First PAH value taken from (2), second PAH value taken from (3). All OC field values taken from (1).

^d Second field value for HCB and α-HCH extrapolated from Equation 1 plots of field data using slope $m' = -\Delta H_{V,L}/2.3R$ as described in (1).

^e Includes trans- + cis-chlordane + trans-nonachlor.

TABLE IV. Saturation Vapor Pressures of Test Compounds

	melting	vapor pressure (torr, 20°C) ^a	
	point (°C)	p_L^0	p_S^0
phenanthrene	101	6.1×10^{-4}	9.3×10^{-5}
anthracene	216	4.1×10^{-4}	4.3×10^{-6}
fluoranthene	375	4.2×10^{-5}	5.1×10^{-6}
pyrene	393	7.5×10^{-5}	3.2×10^{-6}
hexachlorobenzene	230	1.6×10^{-3}	1.2×10^{-5}
α -HCH	159	6.3×10^{-4}	2.5×10^{-5}
γ -HCH	112	2.4×10^{-4}	2.8×10^{-5}
<u>trans</u> -chlordane	106	2.9×10^{-5}	3.9×10^{-6} ^b
<u>cis</u> -chlordane	106	2.2×10^{-5}	3.0×10^{-6} ^b
p,p'-DDE	89	1.2×10^{-5}	2.5×10^{-6}
p,p'-DDT	109	1.2×10^{-6}	1.6×10^{-7}

^a Average p_S^0 of values reported in the literature and summarized in (31), except for the chlordanes. p_L^0 were estimated from p_S^0 using Equation 3, except for the chlordanes, whose p_L^0 were determined using a GC method (31,32).

^b Estimated from p_L^0 using Equation 3.

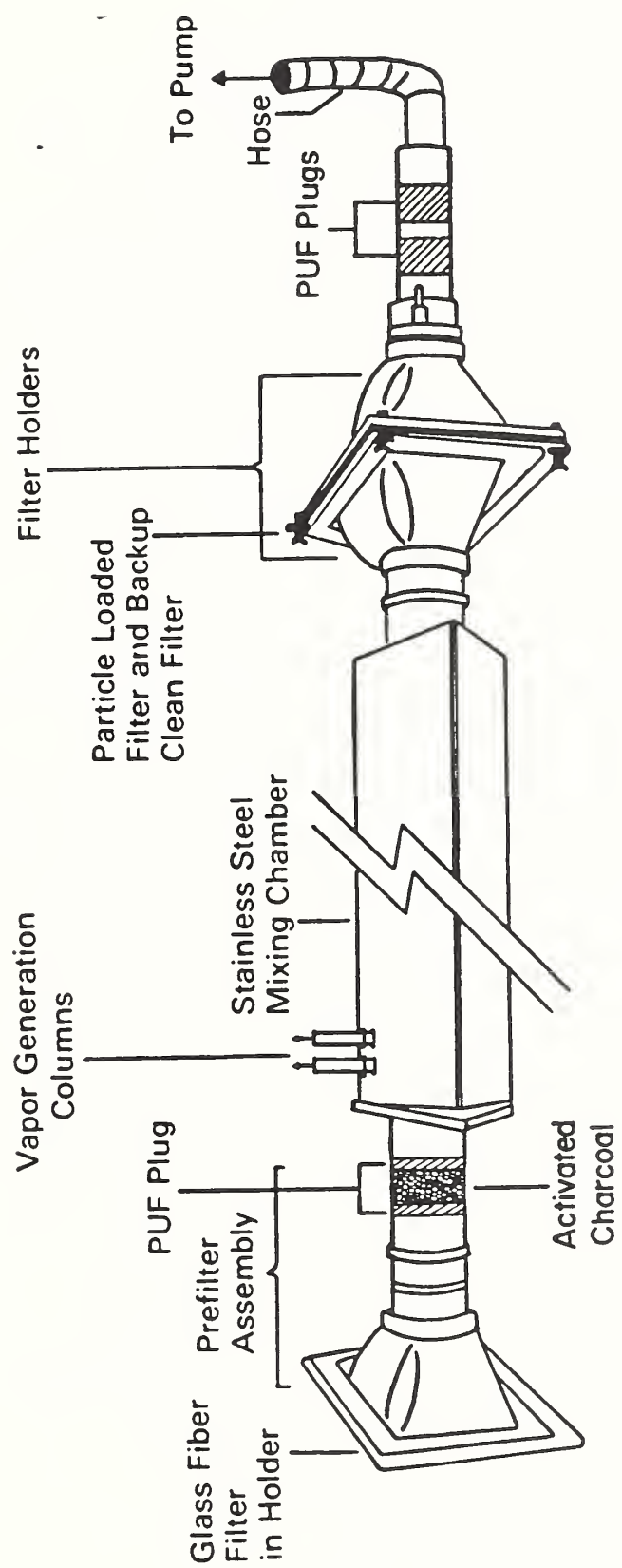
FIGURES

1. Laboratory system for equilibrating particle-loaded filters with SOC vapors.
2. Apparatus used to generate vapor-phase SOC.
3. Changes in vapor concentration (C_A) with air volume in laboratory equilibration system.
4. Concentration of particle-adsorbed OC (C_P) versus concentration in the vapor phase (C_A) for three OC from 6-8 V-P experiments.
5. Log $A(TSP)/F$ at 20°C for OC versus air volume. Equilibration times ranged from about 9 h at 150 m³ to 54 h at 1360 m³. Compound abbreviations given in EXPERIMENTAL section.
6. Log $A(TSP)/F$ at 20°C for PAH versus air volume. Abbreviations given in EXPERIMENTAL section.
7. Relationship between the average laboratory $A(TSP)/F$ and p_S^0 at 20°C for OC. (1 = HCB, 2 = α -HCH, 3 = γ -HCH, 4 = trans-chlordane, 5 = cis-chlordane, 6 = p,p'-DDE, and 7 = p,p'-DDT.)
8. Relationship between the average laboratory $A(TSP)/F$ and p_L^0 at 20°C for OC (■) and PAH (●). OC numbering same as Figure 7.
9. Comparison of laboratory (■) and field (circles) $A(TSP)/F$ at 20°C for OC. Compound identifications 1-7 given in Figure 7, 8 = trans- + cis-chlordanes + trans-nonachlor, 9 = Aroclor 1254. Ranges of field $A(TSP)/F$ are shown for HCB and α -HCH assuming Equation 1 fitted slope $m = -\Delta H_A/2.3R$ (solid circles) and slope

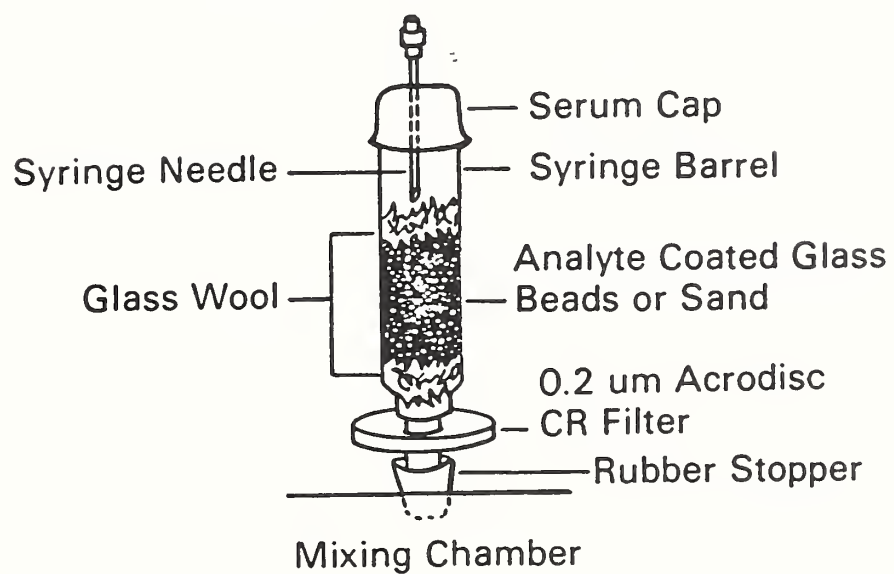
$m' = -\Delta H_{V,L}/2.3R$ (broken circles) as described in ref. (1).

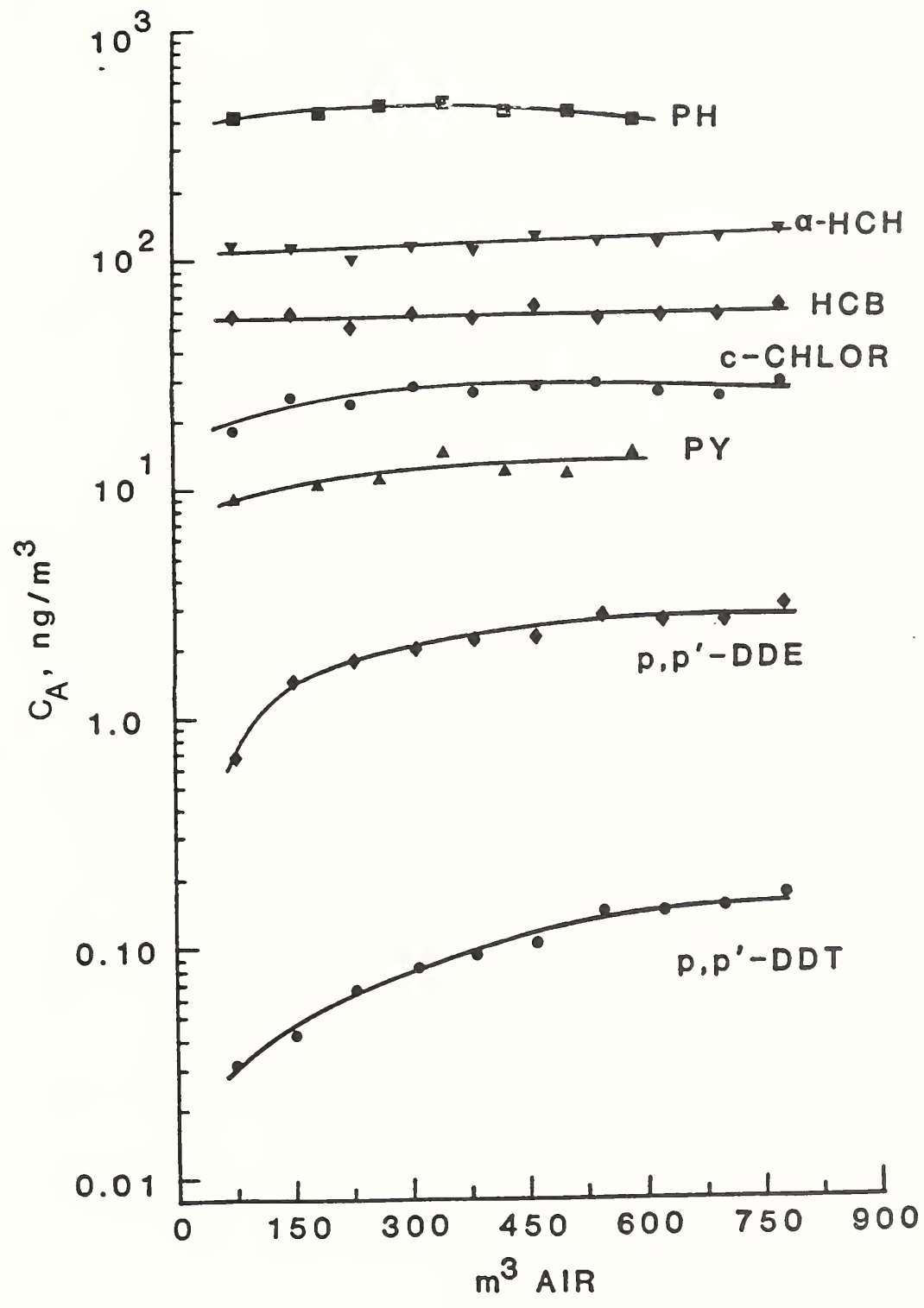
10. Comparison of lab (●) and field (triangles) $A(TSP)/F$ at 20°C for PAH. ▲ = PAH in Tokyo, ref. (3); △ = PAH in Columbia, ref. (2). BkF = benzo(k)fluoranthene, BaP and BeP = benzo(a)- and benzo(e)pyrene.

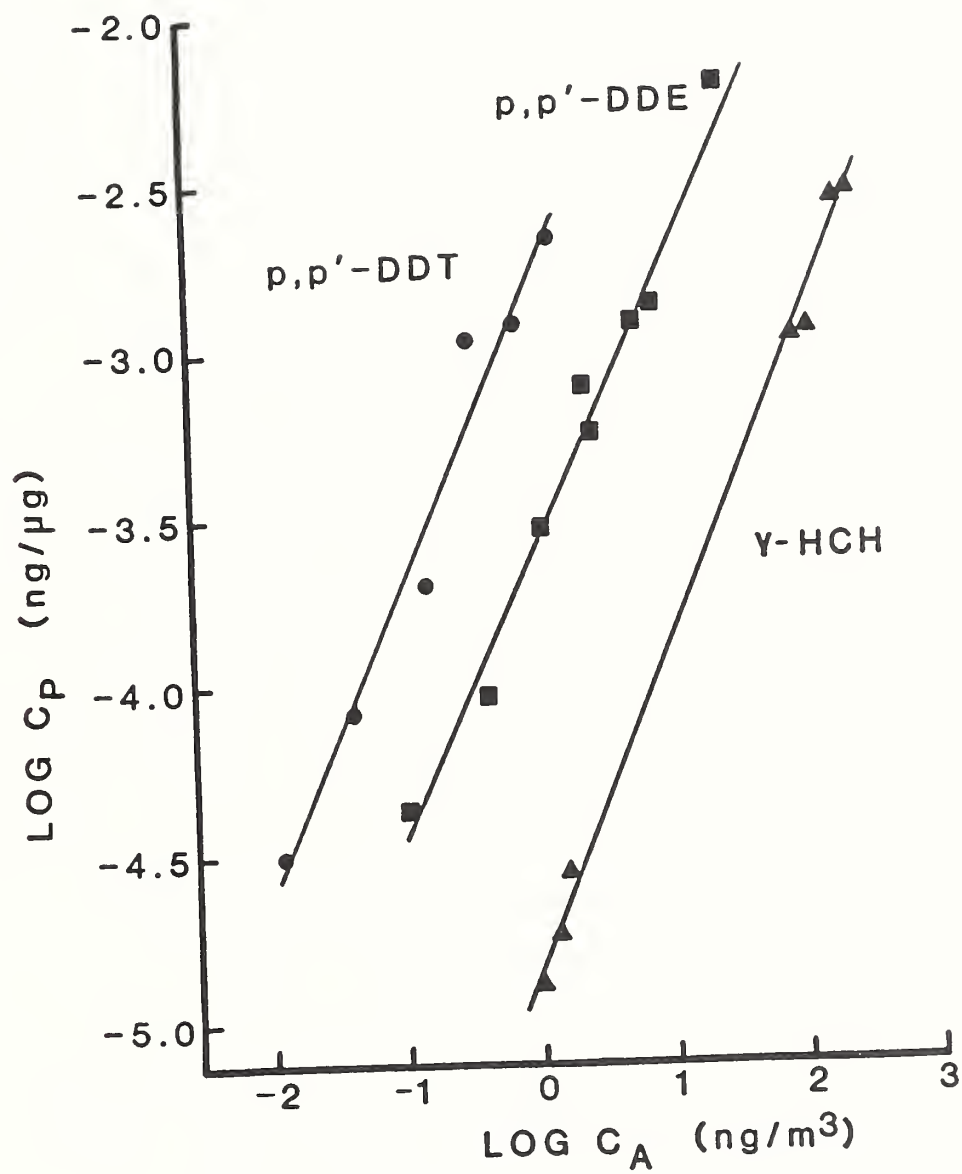
FIG. 1

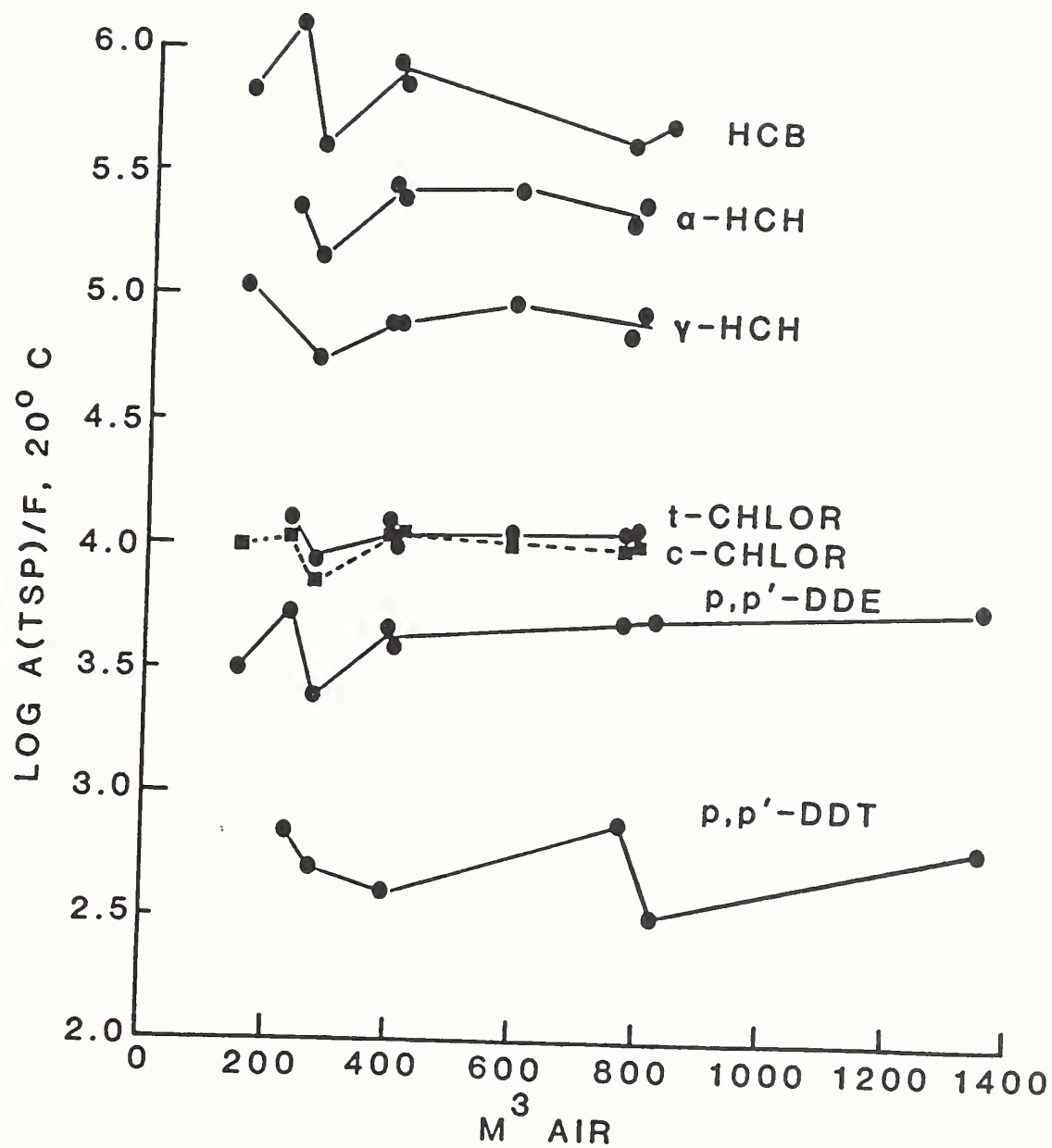


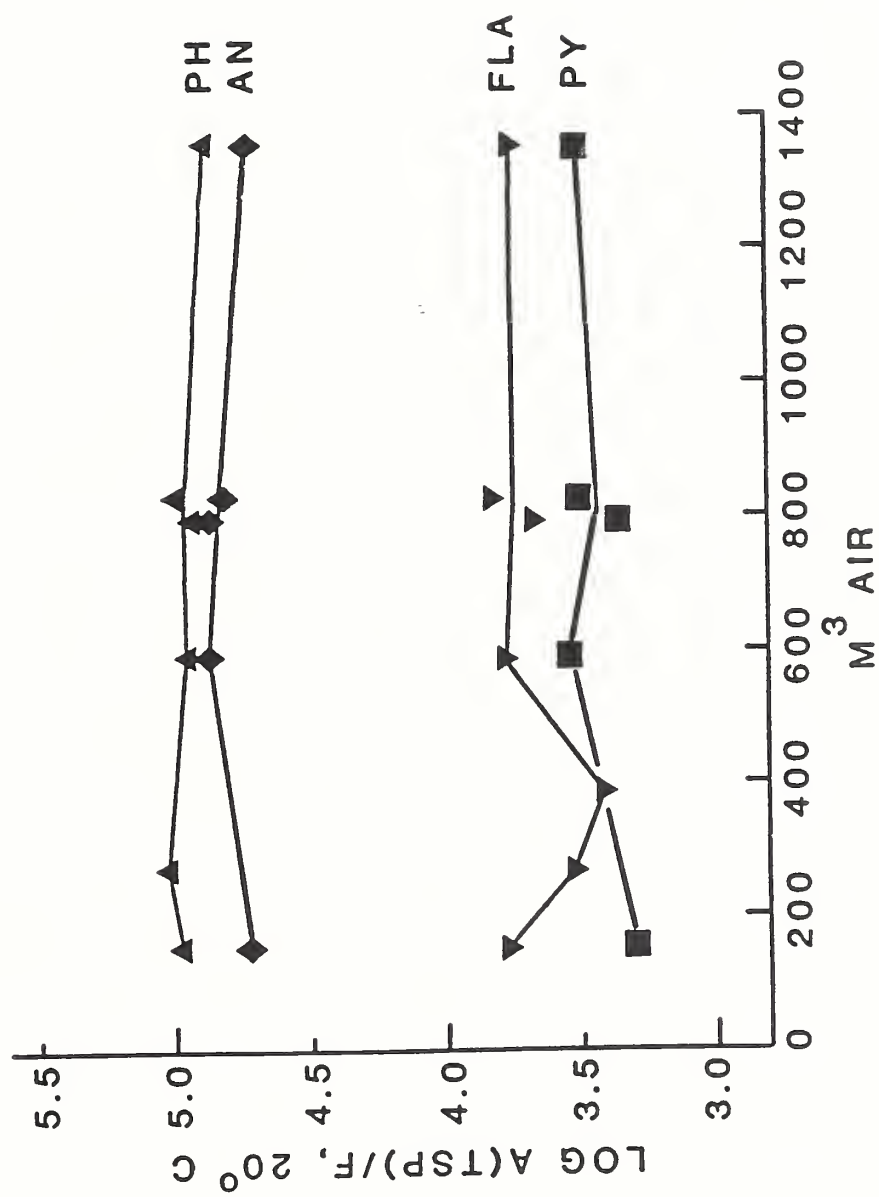
VAPOR GENERATION COLUMN

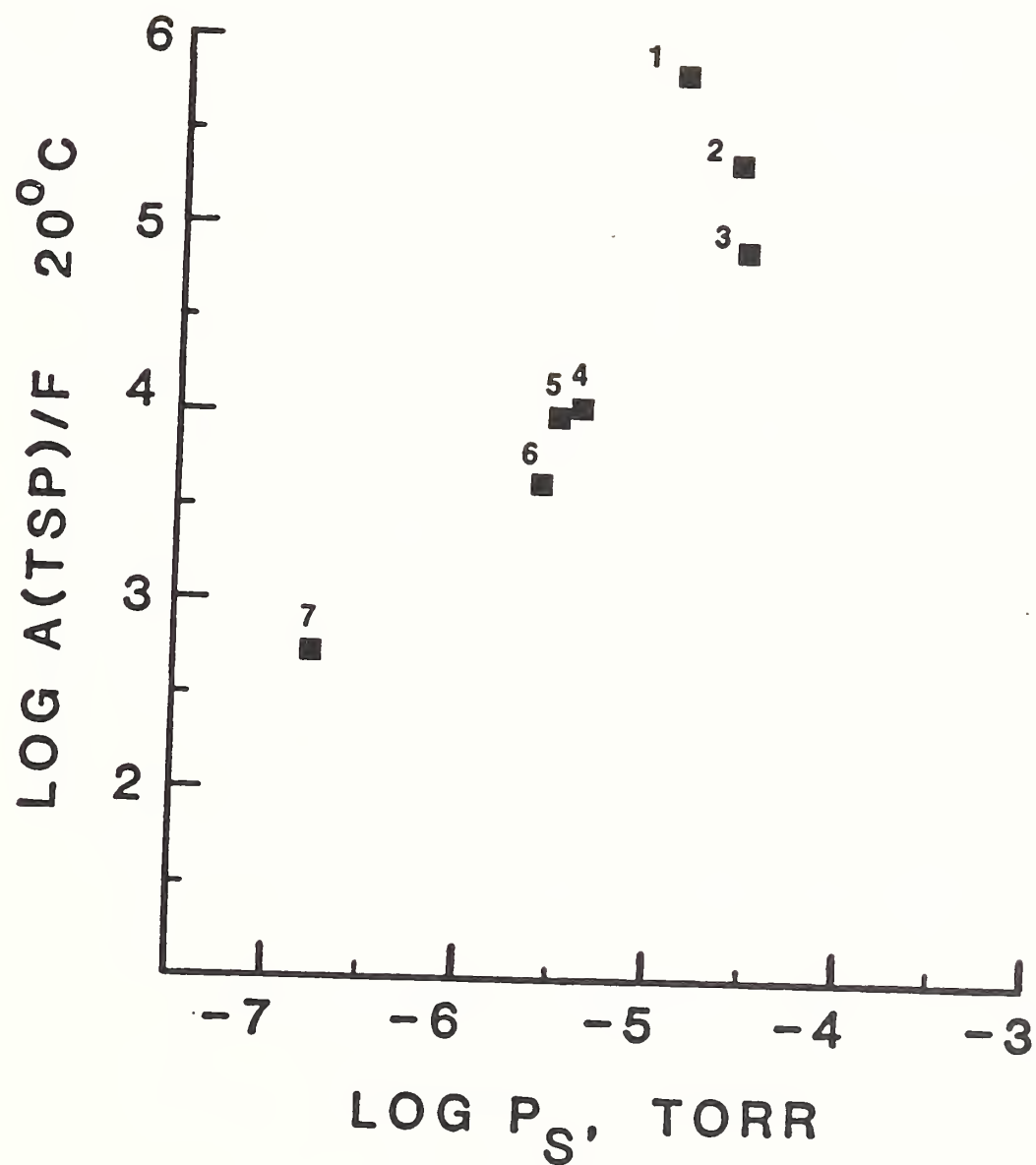


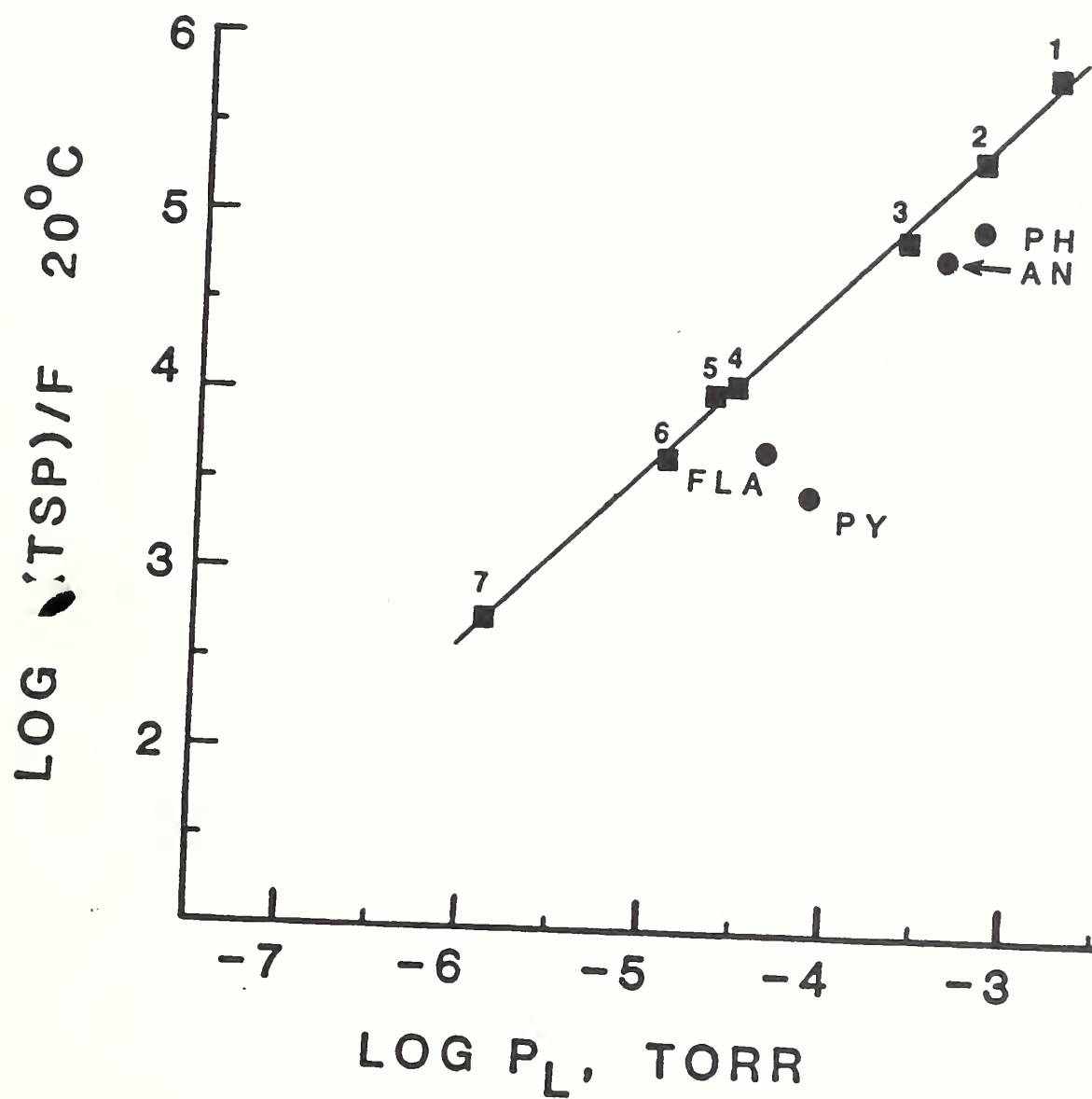


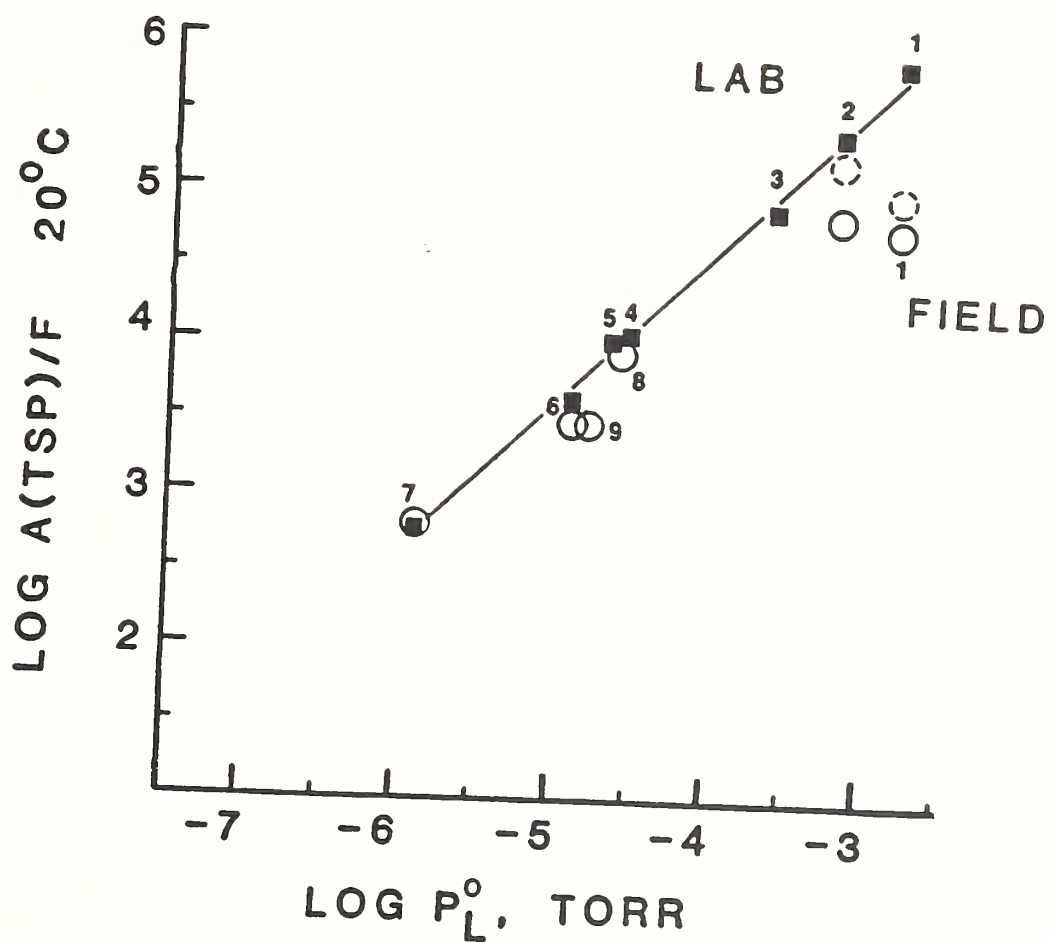




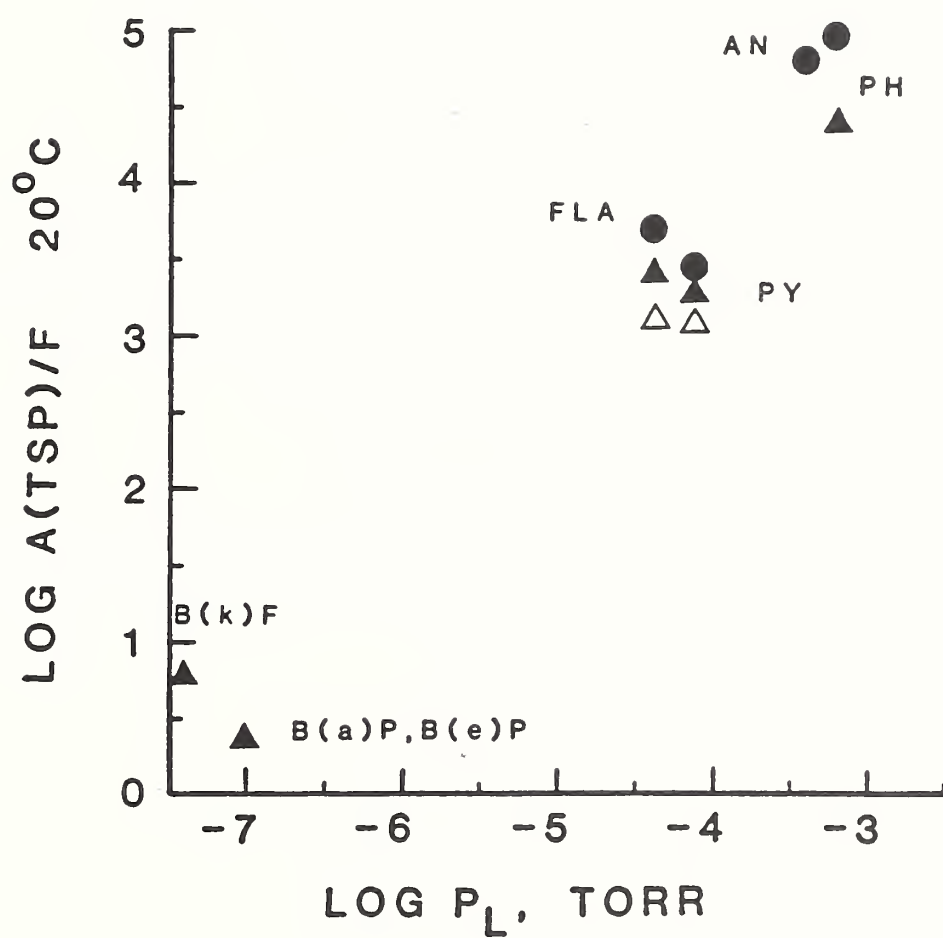












VAPOR-PARTICLE PARTITIONING OF SEMIVOLATILE
ORGANIC COMPOUNDS

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ABSTRACT

Pesticides, polychlorinated biphenyls (PCB), and other semivolatile organic compounds (SOC) exist in air as vapors and adsorbed to particulate matter. Estimates of the vapor-to-particle distribution and factors influencing it were obtained from high-volume sampling experiments using a glass fiber filter to collect particles and an adsorbent trap to collect vapors. Measurements of airborne organochlorine pesticides and PCB in four cities over a wide temperature range were used to determine the partition coefficient $A(TSP)/F$, where A and F are the adsorbent- and filter-retained SOC concentrations (ng/m^3) and TSP is the total suspended particle concentration ($\mu\text{g}/\text{m}^3$). Laboratory determinations of $A(TSP)/F$ were carried out by equilibrating particle-loaded filters at 20°C in an airstream containing controlled SOC vapor concentrations.

Field and laboratory $A(TSP)/F$ agreed well for most organochlorines, with the exception of hexachlorobenzene (HCB). $A(TSP)/F$ was closely correlated with the subcooled liquid vapor pressure (p^0_L) of the SOC, but not with the solid phase vapor pressure (p^0_S). Implications of vapor-particle partitioning to the atmospheric deposition of SOC are discussed.

INTRODUCTION

Semivolatile organic compounds (SOC) such as pesticides, polychlorinated biphenyls (PCB), and polycyclic aromatic hydrocarbons (PAH) are present in the atmosphere as vapors and attached to suspended particles. The vapor-to-particle distribution (V/P) influences atmospheric removal of SOC; for example, heavier PCB having greater fractions in the particle phase are preferentially deposited by washout and dry deposition (1,2). Understanding V/P is also important in designing control systems for stacks, since it is easier to remove particles than vapors. In this article we present results of field and laboratory high volume sampling experiments to investigate the distribution of SOC between the vapor phase and urban air particulate matter.

CHARACTERISTICS OF URBAN AIR PARTICULATE MATTER

Urban aerosols are derived from many sources, including auto exhaust, incineration, industrial emissions, photochemical gas-to-particle conversion, and eolian weathering of soils. Major constituents of urban particulate matter include organic and elemental carbon, sulfate, nitrate, ammonium, silicates, alkali and alkaline earth metals, aluminum, iron, and lead (3-5). Quantifying the contributions of various sources to urban aerosol composition was the subject of an EPA-sponsored workshop in 1982 (6, and other papers in the same issue).

The particle size spectrum ranges roughly from 0.005 μm to 20 μm diameter being limited on the low end by rapid coagulation of smaller particles, and on the high end by gravitational settling (7). The distribution of particle sizes is approximately log normal, and a convenient measure of size is the mass median effective diameter (MMED). For a polydisperse aerosol having MMED = 1 μm , 50% of the total suspended particle (TSP) mass is contained on particles above and below 1 μm . The dispersion is expressed by the geometric standard deviation (σ_g).



Discussions of particle statistics and general characteristics of particles in air are given by Cadle (8), Corn (9), and Whitby (10). MMED and σ_g are remarkably similar for particles in different U.S. cities. A 1970 survey in six cities showed average MMED between 0.4 – 0.8 μm and σ_g between 5 – 10 μm (11). It is important to note, however, that these yearly averages blur large short-term differences. For example, in Cincinnati MMED were 0.44 – 0.48 μm during non-inversion and 1.3 – 2.0 μm during inversion periods (11).

Surface areas of particles collected in Pittsburgh, PA have been measured by Corn *et al.* (12), using a nitrogen adsorption method. Surface areas varied from 1.9 m^2/g in summer to 3.0 m^2/g in winter. To put these into perspective, surface areas of solid adsorbents used to sample organic vapors are in the 20-800 m^2/g range (13). The data of Corn *et al.* (12) were for TSP collected on glass fiber filters, and thus may differ from surface areas of particles suspended in air.

TSP concentrations are determined by their weight on a glass fiber filter following high-volume (hi-vol) sampling. The current primary and secondary 24-h standards for TSP concentrations in ambient air are 75 and 50 $\mu\text{g}/\text{m}^3$ (14). In addition to TSP, two other measures of particle concentration in ambient air are frequently used. A size-selective inlet can be placed over the hi-vol sampler to screen out the very large particles and provide a measure of inhalable particulate matter (IPM) $< 15 \mu\text{m}$. Dichotomous samplers split the particle mass into coarse ($> 2.5 \mu\text{m}$) and fine ($< 2.5 \mu\text{m}$) fractions.

The carbonaceous fraction of urban particulate matter has been the subject of many investigations. Only an overview will be given here, and the reader is referred to several reviews for detailed information (15-21). In 1975 annual average particulate carbon (organic plus elemental) concentrations in 46 U.S. cities ranged from 4-20 $\mu\text{g}/\text{m}^3$ with an overall mean of 10.3 $\mu\text{g}/\text{m}^3$ (21). The range and mean at 20

rural sites were 1.5-6.0 $\mu\text{g}/\text{m}^3$ and 3.7 $\mu\text{g}/\text{m}^3$ (21). Carbon typically comprises 11-21% of TSP (Table 1).

Several methods are used to determine unspiciated carbon. Extractable organic matter or organic carbon (EOM or EOC) is obtained by extracting the particle-loaded filters with an organic solvent and weighing the residues on a microbalance after solvent evaporation (22-24), combustion of the extract to CO_2 in a carbon analyzer (25-28), or, less commonly, by gas chromatographic analysis (29,30). Extraction yields depend on solvent polarity (22-30), and binary mixtures of a polar and non-polar solvent are recommended for highest efficiency (25). Sometimes EOM is fractionated by successive extraction with solvents of different polarities. This scheme can be used to distinguish "primary" organic compounds, which are those directly released into the atmosphere in the particle phase or which condense shortly after introduction, and "secondary" organic compounds, which result from gas-to-particle conversion following chemical reactions of gaseous precursors. Higher proportions of polar fraction EOM resulting from the oxidation of hydrocarbons have been found during pollution episodes and have been correlated with ozone levels (26-28, 31-32).

Total organic carbon (TOC) is determined by dry (21,25,31,32,34) or wet (35) oxidation of a small portion of a particle-loaded filter in a carbon analyzer. Free or elemental carbon (EC) is determined by combustion in a carbon analyzer after prior wet or dry oxidative removal of organic carbon (21,31,34,36,37) or solvent extraction of EOM (26-28), and by absorption or reflectance measurements (38-40).

Table 1 gives some illustrative values of EOM, TOC, and EC as percentages of airborne particulate matter. Several of these were taken from Shah *et al.* (21), who analyzed over 1300 filters from the National Air Surveillance Network filter bank for 1975. The study covered 46 cities and 20 rural sites. Although average EOM contents among cities appear similar, it should be realized that large short-term

differences can occur. For example, during a pollution episode in New Jersey in February, 1983 EOM rose to 30 – 55% of IPM (41). Grosjean and Friedlander (28) found that EOM in Pasadena aerosols varied from 5 – 54%. Also, carbon and individual organic compounds are enriched on the fine fraction from dichotomous samplers (3) and on the smaller aerosols separated by cascade impaction (42-47).

In addition to the above non-specific measures of particulate carbon, a large number of individual organic compounds have been identified and quantified in aerosols by gas and liquid chromatography and GC-MS. The scope of this work can be appreciated from several reviews (15-20). A detailed knowledge of the organic composition of airborne particulate matter is important to understanding pollutant transport, health risks, and natural geochemical cycles.

TABLE 1. Mean Carbon Percentages in Urban Particulate Matter

	Particle Type ^a	EOM	TOC	EC	Reference
Pasadena, CA					
1973	TSP	23			28
annual, 1975	TSP		9.9	4.9	21
Denver, CO					
winter, 1978	TSP		11.3	8.2	3
winter, 1978	FPM		19.6	16.3	3
annual, 1975	TSP		7.0	3.9	21
New York, NY					
	unspecified		8.1	10.2	3
winter, 1976,78	TSP	16			23
summer, 1976-78	TSP	13			23
annual, 1975	TSP		11.8	8.8	21
Newark, NJ					
summer, 1981	IPM	23	10.8	4.5	33
annual, 1975	TSP		9.3	7.3	21

	Particle Type ^a	EOM	TOC	EC	Reference
Elizabeth, NJ					
summer, 1981	IPM	22	8.0	3.3	33
annual, 1975	TSP		9.7	5.7	21
Camden, NJ					
summer, 1981	IPM	22	10.0	5.9	33
annual, 1975			8.0	5.2	21
New Jersey, northeast					
winter, 1983	IPM	33			41
Detroit, MI					
summer, 1981	FPM		22	9.4	48
annual, 1975	TSP		6.8	3.7	21
Chicago, IL					
annual, 1975	TSP		6.3	4.5	21
Miami, FL					
annual, 1975	TSP		6.9	3.6	21
Phoenix, AZ					
annual, 1975	TSP		10.4	3.6	21
Seattle, WA					
annual, 1975	TSP		11.5	8.0	21
Columbia, SC					
annual, 1975	TSP		10.7	7.5	21
Boston, MA					
annual, 1975	TSP		7.3	6.2	21

a) TSP = total suspended particles, IPM = inhalable particulate matter (<15 µm),
FPM = fine particulate matter (<2.5 µm).

VAPOR-PARTICLE DISTRIBUTION OF SOC IN THE ATMOSPHERE

Exchangeable and Non-exchangeable SOC

Although much remains to be learned about the nature of V/P interactions, SOC bound to particles appears to be of two types: a "non-exchangeable" fraction that is strongly adsorbed to active sites on the particles or imbedded within the particle matrix and is not in equilibrium with its vapor phase in the atmosphere, and an "exchangeable" fraction that is more loosely bound and appears to be controlled by the concentration of SOC vapors in air.

Indications that some of the SOC may be non-exchangeable are provided by studies showing that the yield of PAH from the extraction of atmospheric particulate matter depends on the choice of solvent. Some investigators have found that aromatic and polar solvents recover more PAH than non-polar solvents like hexane or cyclohexane (49-51), although others have found no significant differences (52). Griest *et al.* (53) reported difficulty recovering PAH adsorbed on fly ash. Eiceman and VanDiver (54) used gas chromatographic experiments to investigate the equilibrium between PAH vapors and fly ash. Irreversible adsorption occurred at low PAH concentrations, but once a layer of PAH had become attached to the particles, additional PAH were adsorbed reversibly.

Nearly a decade ago Junge (55) considered the situation of the exchangeable fraction, and presented a theoretical model of physical adsorption to aerosols. The fraction of particle-bound SOC (ϕ), solute vapor pressure (p^0), and the particle surface area per unit volume of air (θ) available for adsorption were related through:

$$\phi = c\theta/(p^0 + c\theta) \quad \text{Equation 1}$$

From this model Junge prepared plots of ϕ vs. θ for compounds having p^0 between $10^{-4} - 10^{-8}$ torr. Over the range of θ in urban air, a compound having $p^0 = 10^{-6}$ torr might be expected to be 20 – 80% in the particle fraction. As we will show later, this is similar to experimental estimates in urban air.

Problems with Determining the Exchangeable Fraction

Direct determination of the vapor-to-particle (V/P) ratio in ambient air is an experimentally challenging problem that has not yet been solved. Aerial concentrations of SOC are usually low, on the order of nanograms or picograms per cubic meter, so large volumes of air must be sampled to obtain enough material for analysis. The common technique for preconcentrating SOC is to draw several hundreds to thousands of cubic meters of air through a glass or quartz fiber filter followed by a solid adsorbent trap (13), and the apparent V/P is operationally defined by the adsorbent-retained to filter-retained ratio (A/F).

How closely A/F represents V/P is uncertain. Many investigators feel that A/F overestimates V/P because of the "blow-off effect": stripping of SOC from particles on the filter by the flowing airstream. It is also possible that the particle mass on the filter acts as an adsorbent, leading to an underestimation of V/P. Field collections using different sampling times and different types of filters have provided evidence for each process, although blow-off losses are more commonly reported. Several studies are referenced in (24,45,56-59), and are reviewed briefly in (13).

A limitation of field investigations is that aerial concentrations and temperatures change during the normal sampling period of 24 h or longer. The temperature effect is especially important, since vapor pressures of SOC nearly double with a 5°C increase. Whether blow-off losses or adsorption gains are observed will depend on how and when these variables change during a sampling period. For example, what is deposited on the filter at night may be desorbed again in the heat of the next day. The situation with PAH is complicated by the fact that degradative losses may also occur (60-66).

EXPERIMENTAL MEASUREMENT OF A/F

Field Investigations

Despite the problems mentioned above, field A/F provides insights to the factors influencing vapor-particle interactions in the atmosphere. Investigations of many classes of SOC (PAH, n-alkanes, fatty acids, phthalates, and organochlorines) have shown that, within a homologous series, A/F decrease with increasing molecular weight (1,45,57,67-75). Higher proportions of filter-retained SOC have also been noted for samples collected in winter compared to summer (57,68,70-73,76). Volatility is therefore a major factor controlling adsorption of SOC to atmospheric particulate matter.

Yamasaki *et al.* (73) were the first to quantitatively relate A/F to temperature and particle concentration. Samples were taken over 24-h periods for a year in Tokyo using a glass fiber filter (GFF) to collect particles followed by a polyurethane foam (PUF) column to adsorb vapors. A/F of individual PAH were related to average sampling temperature (T, kelvin) and the TSP concentration by:

$$\text{Log A(TSP)/F} = m/T + b \quad \text{Equation 2}$$

This equation, which is essentially the same as Junge's relationship (Equation 1, see APPENDIX), was successful in describing A/F of PAH in urban air. Regression fits to Equation 2 gave $r^2 \geq 0.8$ for most PAH. The Tokyo samples are the best available data on the adsorption of PAH to ambient air particulate matter. Temperatures were fairly constant, varying by only 2.2 – 2.5°C over each collection period, so non-equilibrium effects caused by changes in vapor pressure with temperature were minimized.

Keller and Bidleman (71) collected EOM and PAH in Columbia, SC under conditions where the diurnal temperature changes were much larger, on the order of 10 – 20°C. Nevertheless, A/F partitioning of EOM, fluoranthene, and pyrene

followed Equation 2, and the parameters m and b were reasonably close to those of the Tokyo samples.

Recently we carried out some field and laboratory investigations of PCB and organochlorine pesticides partitioning between the vapor phase and urban particulate matter on GFFs. Results of the urban air collection experiments are discussed below, and laboratory equilibration studies are presented in a later section. Experimental details of both are given elsewhere (76,77).

Hi-vol samples were taken in four cities using a GFF backed up by a PUF, Tenax, or XAD-2 trap. The cities and dates of sampling were: Columbia, SC (1977-80); Denver, CO (January 1980); New Bedford, MA (June, 1980); and Stockholm, Sweden (1983-85). Sampling periods were usually 24-48 h. Experiments in the U.S. cities were done to also evaluate adsorbent collection efficiencies for PCB and organochlorine pesticide vapors, and these results, along with analytical methods, are presented in (68,76). A summary of organochlorine and TSP concentrations in the four cities is given in Table 2.

Partitioning of organochlorines between the vapor phase and the particle mass on the GFF was strongly influenced by volatility. A chromatogram of the PCB-containing fraction of a Stockholm air sample is shown in Figure 1. Higher proportions of the less volatile SOC can be seen on the GFF compared to the PUF trap, and even within the Aroclor 1254 pattern the heavier components are enriched on the GFF.

Plots of Equation 2 are shown in Figure 2 for Aroclor 1254 and alpha-hexachlorocyclohexane (alpha-HCH). Aroclor 1254 A/F were obtained in all four cities. Alpha-HCH was measureable on the GFF only at low temperatures, and so all alpha-HCH results are from Denver and Stockholm. Plots of Equation 2 were also made for p,p'-DDE (DDE), p,p'-DDT (DDT), chlordane, and hexachlorobenzene (HCB) (76). The DDE, DDT, and chlordane data were from Columbia, Denver, and

Stockholm, but A/F of the more volatile HCB were determined only in the latter two cities.

Regression parameters for the organochlorines are given in Table 3, along with best-fit A(TSP)/F values at 20° and 0°C. The individual points in Figure 2 and similar plots show some variability, but the r^2 in the 0.88 – 0.90 range for Aroclor 1254, DDE, DDT, and chlordane compare well with the PAH r^2 of Yamasaki *et al.* (73). Lower r^2 were obtained for HCB and alpha-HCH because of the smaller number of data points and greater scatter. As mentioned above, HCB and alpha-HCH residues on the GFFs approached the detection limits except at the coldest temperatures.

Several other factors may have contributed to the scatter in the Equation 2 plots: Day-to-night temperature fluctuations over the collection periods may have caused blow-off losses or adsorption gains to particles on the GFF during individual experiments. It is also likely that organochlorine concentrations in the air varied over an experiment. Data in the Equation 2 plots were obtained from measurements in several cities over 8 years, and were influenced by local differences in particle size distribution, surface area, and content of carbonaceous material. The influence of relative humidity (RH) on SOC adsorption to atmospheric particles is unknown and, although not measured, RH probably varied substantially over the course of these experiments. Adsorption of nonpolar SOC might be expected to decrease at high humidity because of the displacing effect of water molecules. Chiou and Shoup (78) found that the uptake of chlorobenzene vapors by soil was greatly diminished at high humidities. Spencer *et al.* (79,80) incorporated lindane and dieldrin into dry soil and measured an increase in their partial pressures when the soil was hydrated. It should be mentioned, however, that urban aerosols have a much higher organic content than most soils, and humidity effects in soil adsorption studies may not apply to atmospheric particulate matter. Considering the large list of variables, it is

surprising that the correlations are as good as they are. Volatility thus stands out as the primary factor governing SOC partitioning to urban aerosols.

If the interaction between SOC vapors and atmospheric particulate matter is relatively weak, physical adsorption, the slope (m) of Equation 2 plots should be the same as the slope (m') of $\log p^0$ vs. $1/T$ (see APPENDIX). Equation 2 slopes for PCB, DDE, DDT, and chlordane were in the -4700 to -5900 range (Table 3), which are close to m' for most high molecular weight SOC. Heats of adsorption (ΔH_A), calculated from slopes m , were at most 2-4 kcal/mol greater than heats of vaporization of the subcooled liquid phase ($\Delta H_{V,L}$) for PCB, DDE, DDT, and chlordane (76). Yamasaki *et al.* (81) also found that ΔH_A were only 2-4 kcal/mol greater than $\Delta H_{V,L}$ for PAH.

Table 2. Average Organochlorine^a and TSP Levels in Four Cities

City	ng/m ³						µg/m ³
	PCB	DDE	DDT	Chlordane	HCH	HCB	TSP
Columbia, SC	1.5	0.093	0.048	1.3	0.9	0.29	53
Denver, CO	0.45	0.021	0.043	0.063	0.22	0.24	175
New Bedford, MA (landfill)	9.3						193
Stockholm, Sweden	0.067	0.0034	0.0061	0.010	0.40	0.065	34

a) PCB = Aroclor 1254, DDE and DDT = p,p'-DDE and p,p'-DDT, Chlordane = cis- + trans-chlordane + trans-nonachlor, HCH = alpha-hexachlorocyclohexane, HCB = hexachlorobenzene

The strong dependence of A/F on temperature suggested a general relationship based on SOC volatility. Vapor pressures of the organochlorines in this work and the PAH investigated by Yamasaki *et al.* (73,81) span four orders of magnitude (Table 4). Figure 3 shows a log-log plot of the best-fit A(TSP)/F at 20°C (Table 3) vs. the subcooled liquid vapor pressure (p^0_L) of the SOC. Differences between p^0_L and the solid-phase vapor pressure p^0_S will be discussed in the next section. A(TSP)/F have been plotted for the organochlorines, and for PAH using data from Yamasaki *et al.* (73) and Keller and Bidleman (71).

Since the uncertainties in the Equation 2 parameters for alpha-HCH and HCB were larger than for the other organochlorines, we have also extrapolated A(TSP)/F at 20°C from data obtained at sub-zero temperatures (where filter-retained quantities were easily measureable), assuming the slope (m') of the $\log p^0_L$ vs $1/T$ relationship (76) (see APPENDIX). The bars in Figure 3 thus represent the range of A(TSP)/F at 20°C obtained using two different slopes in Equation 2.

Table 3. Equation 2 Regression Parameters for Organochlorines

	m	b	r^2	n	Log A(TSP)/F ^a	
					0°C	20°C
alpha-HCH	-2755	14.286	0.574	11	4.194	4.883
HCB	-3328	16.117	0.687	8	3.925	4.758
Aroclor 1254	-4686	19.428	0.885	34	2.265	3.436
Chlordane	-4995	21.010	0.901	18	2.711	3.960
p,p'-DDE	-5114	21.048	0.881	15	2.320	3.598
p,p'-DDT	-5870	22.824	0.885	18	1.320	2.788

a) Units of A(TSP)F are ng SOC/m³ air ÷ ng SOC/μg particles.

A/F of both classes of pollutants were closely related to p_L^0 , but different lines were obtained for organochlorines and PAH. At given p_L^0 , the proportion of PAH on particulate matter was higher than for organochlorines. This behavior is currently under investigation, but as of now we suggest two possible explanations: PAH are planar molecules, and may be more strongly adsorbed than most of the organochlorines, only one of which is flat (HCB). It is also likely that urban particulate matter contains some non-exchangeable PAH, bound to highly active sites or trapped within the particles, which is extracted with solvent during analysis and counted along with the exchangeable PAH.

It is interesting to compare field A/F with those predicted by Junge (55). From Figure 3, A(TSP)/F in urban air are about 500 and 50 for an organochlorine and PAH having $p_L^0 = 10^{-6}$ torr. Assuming TSP = $60 \mu\text{g}/\text{m}^3$, $\phi = F/(A + F) = 0.11 - 0.55$ (11 - 55%) for organochlorines and PAH, respectively. These agree reasonably well with $\phi = 20 - 80\%$, estimated from Junge's diagram (55) over the particle concentration range in urban air.

Laboratory Equilibration Experiments

Some of the problems with field experiments can be circumvented by investigating vapor adsorption to particles in the laboratory where temperature, RH, and vapor concentrations can be controlled. We have designed a system for equilibrating particle-loaded filters with SOC vapors that is similar to a hi-vol sampling train (77) (Figure 4). Clean air was supplied by drawing laboratory air through a GFF and adsorbent cartridge. SOC vapors were bled into a stainless steel chamber from coated sand generator columns fitted with $0.2 \mu\text{m}$ Acrodisc CR filters on the outlet ends. The vapors were mixed with the hi-vol air stream ($0.3 - 0.5 \text{ m}^3/\text{min}$), passed through a particle-loaded filter backed up by a clean filter, and

finally through a PUF trap which stripped the vapors from the airstream and preconcentrated them for analysis.

Equilibration experiments were carried out by exposing two 20 x 25-cm GFFs to SOC vapors at 20°C and RH = 58- 73% for varying times and air volumes. The front filter was loaded with approximately 100-250 mg urban air particulate matter by hi-vol sampling in Columbia for 48 h. The back filter was a blank to correct for vapor adsorption to the filter matrix itself. Since only a small fraction of the total SOC vapor input was retained by the particles, the vapor concentration seen by the back filter was considered the same as that seen by the front filter. The PUF trap behind the filters was changed every 2-3 h and analyzed to determine changes in vapor concentration with time. At the end of the experiment, the filters were extracted with dichloromethane and analyzed for organochlorines by GC-ECD. Details of the analytical methods are given in (77). The experiments yielded vapor-particle partition coefficients at 20°C, $A(TSP)/F$, expressed in the units $\text{ng SOC/m}^3 \text{ air} \div \text{ng SOC}/\mu\text{g particles}$.

Eight runs were carried out with organochlorine pesticides over a range of concentrations and equilibration times (air volumes). Conditions are summarized in Table 5. Three lots of particulate matter were used, collected from Columbia air on October 31 - November 1, 1984; April 2-5, 1985; and August 26-28, 1985.

Changes in vapor concentration behind the exposed filters for one run of 770 m³ (about 30 h) are shown in Figure 5. Concentrations of the more volatile organochlorines remained constant over the entire run, whereas a lag time of several hours was noted before the heavier organochlorines reached stable levels. In these cases $A(TSP)/F$ were calculated using plateau vapor concentrations; *e.g.*, the mean of the last four p,p'-DDT points in Figure 5.

Experiments carried out over 9-54 h (150 – 1360 m³ air) showed that a steady state was reached quickly between the particles on the GFF and vapors in the

Table 4. Vapor Pressures of Organochlorines and PAH, torr (20°C)^{a,b}

	mp, °C	p ^o _S	p ^o _L
Organochlorines			
alpha-HCH	159	2.5 × 10 ⁻⁵	6.3 × 10 ⁻⁴
gamma-HCH	112	2.8 × 10 ⁻⁵	2.4 × 10 ⁻⁴
HCB	230	1.1 × 10 ⁻⁵	1.4 × 10 ⁻³
Aroclor 1254 ^c			1.4 × 10 ⁻⁵
trans-chlordane	106	3.9 × 10 ⁻⁶	2.9 × 10 ⁻⁵
cis-chlordane	106	3.0 × 10 ⁻⁶	2.2 × 10 ⁻⁵
trans-nonachlor			1.7 × 10 ⁻⁵
p,p'-DDE	89	2.6 × 10 ⁻⁶	1.3 × 10 ⁻⁵
p,p'-DDT	109	1.6 × 10 ⁻⁷	1.3 × 10 ⁻⁶
PAH			
phenanthrene	101	9.5 × 10 ⁻⁵	6.2 × 10 ⁻⁴
anthracene	216	4.3 × 10 ⁻⁶	4.1 × 10 ⁻⁴
fluoranthene	111	5.1 × 10 ⁻⁶	4.2 × 10 ⁻⁵
pyrene	156	3.1 × 10 ⁻⁶	7.3 × 10 ⁻⁵
benzo(k)fluoranthene	217	3.9 × 10 ⁻¹⁰	3.7 × 10 ⁻⁸
benzo(e)pyrene	179	2.4 × 10 ⁻⁹	9.6 × 10 ⁻⁸
benzo(a)pyrene	177	2.4 × 10 ⁻⁹	9.2 × 10 ⁻⁸

- a) p^o_S are averages of literature values, compiled as an appendix to (82), except for cis- and trans-chlordane. p^o_S of these two compounds were estimated from p^o_L using Equation 3.
- b) p^o_L were calculated from literature p^o_S using Equation 3, except for Aroclor 1254 (which is a liquid at 20°C), cis- and trans-chlordane, and trans-nonachlor. p^o_L of the latter three compounds were determined using the GC method described in (82).
- c) p^o_L of Aroclor 1254 was estimated by summing the partial pressures of PCB congeners (83) that were included in the air sample analysis.

airstream (Figure 6). Residues on backup GFFs averaged 10% or less of those on the particle-loaded GFFs. Thus, adsorption on the glass fiber filter itself was slight compared to adsorption by the particles. Backup GFF residues were subtracted from those on the front filter when calculating $A(\text{TSP})/F$. Vapor concentrations of some SOC (Table 5) were varied by 1-2 orders of magnitude without affecting $A(\text{TSP})/F$. The constancy of $A(\text{TSP})/F$ (Figure 6) is rather remarkable, considering that three different lots of urban particulate matter were used for the experiments.

An important question is whether vapor-particle partitioning is controlled by the vapor pressure of the subcooled liquid (p_L^0) or the crystalline solid (p_S^0). The two vapor pressures can be interconverted through:

$$\ln p_L^0/p_S^0 = \Delta S_f(T_m - T)/RT \quad \text{Equation 3}$$

where T_m and T are the melting point and ambient temperatures (kelvin) (84).

Estimates of the entropy of fusion (ΔS_f) for rigid molecules range from 10-17 cal/deg-mol, with a most likely value of 13.5 cal/deg-mol (85). The range of experimentally determined ΔS_f for 16 PCB congeners was 9.8-16.6 (mean = 13.1) cal/deg-mol (86). We used 13.5 cal/deg-mol ($\Delta S_f/R = 6.79$) in Equation 3.

Differences between p_S^0 and p_L^0 increase rapidly with melting point. At 20°C a low-melting point substance like p,p'-DDE (mp 89°C) has p_L^0 five times higher than p_S^0 , whereas the difference is a factor of 130 for HCB (mp 230°C) (Table 4). Vapor pressure is reduced over a solid relative to its subcooled liquid because of the crystal lattice energy. When individual solute molecules condense on an indifferent surface (*i.e.*, physical adsorption), no solute crystal lattice is present and the adsorption might be expected to be controlled by p_L^0 rather than p_S^0 . Several lines of evidence indicate that some environmentally important phase distributions are controlled by liquid-phase physical properties: Yamasaki *et al.* (81) found that the heats of PAH adsorption onto urban air particulate matter were close to the subcooled liquid PAH heats of vaporization. Breakthrough of PAH and

organochlorine vapors on solid adsorbent collection traps is governed by p^0_L rather than by p^0_S (87,88). Octanol-water partition coefficients (K_{ow}) and bioconcentration factors (BCF) are inversely related to the water solubility of the subcooled liquid phase (89).

Table 5. Range of Conditions and Mean $A(TSP)/F$ for Laboratory Vapor-Particle Equilibration Experiments.

Compound	Experiments	Vapor Concentration, ng/m^3	Air Volume m^3	Log $A(TSP)/F^a$
alpha-HCH	7	53-160	230-790	5.362
gamma-HCH	7	1-252	150-790	4.908
HCB	7	30-87	150-830	5.833
trans-chlordane	7	17-56	230-790	4.041
cis-chlordane	8	9-40	150-790	4.000
p,p'-DDE	8	0.1-27	150-1360	3.653
p,p'-DDT	6	0.013-1.5	230-1360	2.748

a) Units of $A(TSP)/F$ are $ng\ SOC/m^3\ air \div ng\ SOC/\mu g\ particles$. All experiments were done at 20°C. Particle weights on the GFF ranged from 100 – 250 mg.

Figures 7 and 8 show log-log plots of $A(TSP)/F$ vs. p^0_S or p^0_L . The points in Figure 7 show a good deal of scatter, especially for the higher melting compounds alpha-HCH and HCB, whereas the correlation in Figure 8 is excellent ($r^2 = 0.998$). This, along with field data (Figure 3), supports p^0_L as the relevant property for describing vapor-particle equilibria in the atmosphere.

$A(TSP)/F$ from field and laboratory experiments are compared in Figure 9. The agreement is very good for the chlordanes, DDE, and DDT, but less so for alpha-HCH and HCB. As mentioned earlier, filter-retained quantities of these two volatile

organochlorines were difficult to determine except at very cold temperatures, and the uncertainties in extrapolating Equation 2 plots to 20°C were large. This may in part account for the field and laboratory differences seen in Figure 9. The agreement for alpha-HCH can be improved by assuming a slope for its Equation 2 plot equal to m' , the slope of the p^0_L temperature dependence (76). However the situation of HCB is not greatly improved. An alternative explanation may lie in the different ways that SOC become bound to particles in urban air vs. in laboratory equilibration experiments. Vapors introduced in the latter experiments probably condensed on the surface of the particles on the GFFs. SOC on filters from field collections also included material trapped within the particle matrix or strongly adsorbed to active sites, *i.e.* "non-exchangeable" SOC. Differences between the laboratory and field $A(TSP)/F$ might be expected to be greatest for SOC that become incorporated into the particles at the time of formation and less for SOC that condense onto the particles later in their lifetime. SOC in the former category include combustion-derived compounds such as PAH and HCB, and it is for HCB that we found the greatest difference between laboratory and field $A(TSP)/F$. Organochlorine pesticides probably enter urban air as vapors via transport from agricultural areas or by evaporation from treated areas within the city (*e.g.* chlordane, used in structural termite control) and then condense onto urban aerosols. For these compounds, laboratory and field $A(TSP)/F$ agree quite well.

RELATIONSHIP OF VAPOR-PARTICLE PARTITIONING TO PRECIPITATION SCAVENGING.

Atmospheric deposition contributes substantially to pollutant loadings in the Great Lakes. Several investigators have documented aerial transport and flux of SOC (PCB, pesticides, PAH) to the Great Lakes (2,90-105). Hydrocarbons and fatty acids have also been found in precipitation from the midwestern U.S. (106). Analysis of PCB in ice cores from Lake Huron provided an integrated measure of wintertime

deposition (107). Atmospheric deposition is the most likely explanation for the presence of PCB, pesticides, and dioxins in fish and sediments from Lake Siskewit, a landlocked lake located on Isle Royale, Lake Superior (100,108), and for DDT (109) and toxaphene (110) in peat cores from Minnesota, Maine and southeastern Canada.

Atmospheric fluxes of SOC occur by wet and dry deposition of gases and particles, and exchange of gases across the air-water interface. An excellent overview of these processes and their role in contributing SOC to the Great Lakes has been given by Eisenreich *et al.* (101). V/P has an important influence on the atmospheric removal of SOC. Vapor washout is governed by Henry's Law constant (H), an air-water partition coefficient that may be calculated from the ratio of vapor pressure to water solubility. Other SOC that have substantial fractions in the particle phase and/or Henry's law constants unfavorable for vapor scavenging are removed by particle washout.

A model for SOC washout incorporating vapor and particle scavenging was presented by Pankow *et al.* (111), and Ligocki *et al.* (112,113). The overall washout ratio, $W = \text{mass SOC/volume rain} \div \text{mass SOC/volume air}$, is related to the washout ratios of vapors ($W_v = RT/H$) and particles (W_p), and the fraction of particulate SOC (ϕ).

$$W = RT/H(1-\phi) + W_p\phi \quad \text{Equation 4}$$

Equation 4 is a simple equilibrium model that ignores the complications of meteorology. For details of the physical process of precipitation scavenging, the reader is referred to several articles (115-119). The dominant rain scavenging mechanism depends on the relative magnitude of W_v , W_p , and ϕ . Ligocki *et al.* (112,113) collected rain and concurrent air samples in Portland, OR and found that 2-4 ring PAH were washed out as vapors. Field W_v were 3-6 times higher than those predicted from H at 25°C, but if H at the appropriate rain temperatures were used, the agreement between field and equilibrium values was a factor of two or better.

Other compounds removed mainly by vapor scavenging are HCH (112,113,120,121) and phenols (122). SOC for which particle scavenging dominates are PCB and DDT (1,2), PAH of five or more rings (113), and n-alkanes (113,123). Within the suite of PCB congeners, those that are less volatile and have greater fractions on particles are preferentially deposited by rain and dry deposition (1,2).

We will use Equation 4 to estimate the likely mode of wet deposition for toxaphene, an organochlorine pesticide of concern in the Great Lakes. In the three years before its ban in November, 1982, over 30,000 tonnes of toxaphene was applied (124) to soybeans, cotton, grain, and as a cattle dip (125). Toxaphene is translocated from heavy application areas in the southern U.S. to the Great Lakes (103) and eastern Canada (126) and has been found in peat cores from the north central and eastern U.S., and southeastern Canada (110). Toxaphene is a widespread contaminant in fish from the Great Lakes (127) and eastern Canadian marine waters (128). Since toxaphene is carcinogenic in laboratory animals (129), the U.S. Environmental Protection Agency cited potential risks to fish-consuming populations in the Great Lakes and Mississippi Delta regions in their decision to ban toxaphene (125,130). Toxaphene is one of the eleven "critical pollutants" recommended for study of sources and transport by the Great Lakes Water Quality Board (131).

Toxaphene is a complex mixture of chlorinated bornanes and camphenes with a wide range of poorly defined physical properties. Nearly all physical data refer to the technical toxaphene mixture, a waxy semisolid with a melting range of 70-90°C. A brief review of these properties is given in (132). Seiber *et al.* (133) and Murphy *et al.* (134) reported average vapor pressures for the mixture, which are in the 3×10^{-7} - 6×10^{-6} torr range at 20°. Murphy *et al.* (134) also determined the water solubility of toxaphene (0.55 mg/L, or 1.3×10^{-3} mol/m³ assuming an average molecular

composition $C_{10}H_{10}Cl_8$). From the solubility and vapor pressure, $H = 6.1 \times 10^{-6}$ atm-m³/mol can be calculated.

If toxaphene behaves like other organochlorines (Figure 3), about ²~~3~~-17% should be filter-retained at 20° and TSP = 40 µg/m³. This TSP concentration is the geometric mean (GM) found by Andren and Strand (92) over Lake Michigan. For reasons discussed earlier in this article, the filter-retained percentage may or may not represent the true particulate fraction in ambient air, but it is the only estimate we have.

Gatz (135) reported W_p for trace metals, which generally increase with MMED. W_p for Pb and Zn (MMED ~0.7-1.2 µm) were 6.3×10^4 and 1.4×10^5 . SOC are preferentially concentrated on the smaller particles, and MMED for particles containing PAH, alkanes, and organic acids are typically 1-2 µm or less (42,-44,136), so W_p for SOC might be expected to be on the order of 10^5 . Actual field measurements of W_p for SOC are few and variable. Ligocki *et al.* (113) found W_p for n-alkanes in the $1.3-2.2 \times 10^4$ range, and lower values for particulate PAH. W_p for particulate alkanes found by Farmer and Wade (123) were much higher, ranging from $6.0-8.6 \times 10^5$. A $W_p = 1 - 2 \times 10^5$ was selected by Scott (114) for modeling the wet deposition of submicrometer particles.

Assuming $W_p = 1 \times 10^5$ for toxaphene, $\phi = 0.03-0.17$, and $H = 6.1 \times 10^{-6}$ atm-m³/mol, $(RT/H)(1-\phi) = 3.2-3.9 \times 10^3$, $W_p\phi = 0.3-1.7 \times 10^4$, and $W = 2.0 \times 10^4$ to 3.1×10^4 . Vapor scavenging thus accounts for a major share of toxaphene deposition. Particle scavenging could be of ^{25%}equal importance or only ^{33%}one-fifth of the total, depending on the choice of toxaphene vapor pressure (controlling ϕ). The overall W are also sensitive to the choice of W_p , and as discussed above, a great deal of uncertainty exists concerning the magnitude of W_p for particulate SOC.

The predicted W from toxaphene physical properties and V/P partitioning may be compared with field values. Between 1976-78 we measured the rainfall flux of

toxaphene and other organochlorines to North Inlet estuary, a high salinity marsh on the South Carolina coast that receives little fresh water input other than through rainfall (1, 137). Toxaphene was the most abundant pesticide in precipitation; loading to the estuary was estimated at 4.6 kg/ha from June-September, 1977 (137). Concurrent air samples were taken with 16 rain events at North Inlet, and two air-rain sample pairs were collected from shipboard about 300 km off the coast of Delaware. Toxaphene W ranged from <0.13 - 7.2×10^5 . In our original articles (1,137), the arithmetic mean (AM) W was given as 2.3×10^5 . This mean is too high for two reasons. First, only positive samples (13 out of 18) were averaged. Second, the distribution of W is log normal, and a better central measure is the geometric mean (GM) (116). The GM gives less weight to a few large values than does the AM. The GM of the 18 North Inlet and shipboard W, including upper limits for samples below the detection limit, was 6.6×10^4 . This is higher than our predicted W of ~~4.5~~^{0.6}

^{2.0} ~~3.1 $\times 10^4$, but certainly the order of magnitude is correct.~~ And the difference argues for a better knowledge of toxaphene physical properties as well as rain scavenging mechanisms for particulate SOC.

The above exercise shows how a model incorporating vapor-particle partitioning can be used to predict precipitation removal mechanisms. Mackay *et al.* (138) recently presented a thorough discussion of wet and dry SOC deposition which includes vapor-particle equilibria.

In closing, it should be mentioned that there may be mechanisms for concentrating SOC in rainfall that are not included in the Equation 4 model. Rain contains surface-active material (20), and the importance of surface films in modifying vapor exchange across the air-drop interface has not been examined. Glotfelty *et al.* (139) collected fog droplets with a rotary impactor in the California San Joaquin valley, a heavy pesticide use area. The filtered fog water and concurrent air samples were analyzed for organophosphate insecticides and a dinitroaniline herbicide. Pesticide concentrations in the fog water were enriched 88-2400 times above equilibrium values predicted from Henry's Law. The

enrichment mechanism has not yet been elucidated, but it seems plausible that a SOC solubility enhancement due to dissolved organic material or partitioning of SOC into surface films on the droplets might be a factor.

CONCLUSIONS

Many uncertainties still remain in our knowledge of vapor-particle interactions in ambient air. A major question, unanswered by either our field or laboratory experiments, is: How closely does A/F represent the true V/P in the atmosphere? It seems likely that the process of collecting particles on a filter will alter their size and surface area distribution from the situation where the particles were floating freely in the atmosphere. It is therefore important to stress that the $A(TSP)/F$ partition coefficients in this work are between vapors and urban air particulate matter on filters, not airborne particles.

Despite this shortcoming, field and laboratory experiments have provided some valuable information about the nature of vapor-particle interactions. Particles on GFFs reach a steady state with SOC vapors within a few hours. A/F partitioning of non-polar compounds appears to be due to simple physical adsorption, controlled by SOC volatility, and the apparent partition coefficient $A(TSP)/F$ is better correlated with p°_L than p°_S .

Implications of the p°_L hypothesis are important for high-melting compounds. For example, p°_S of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) has recently been measured by the gas saturation method (140). At 20°C $p^{\circ}_S = 6.1 \times 10^{-10}$ torr, and if p°_S were controlling V/P in the atmosphere, all the TCDD would be expected to be particle-bound. However the melting point of TCDD is 305°C and p°_L at 20°C is 745 times p°_S , or 4.5×10^{-7} torr. Based on this p°_L , and assuming that TCDD behaves like other organochlorines (Figures 3 and 8), a substantial proportion of the TCDD may exist in the atmosphere in the vapor phase. A better knowledge of vapor-

Particle equilibria and the controlling thermodynamic factors is thus important to our understanding of SOC atmospheric chemistry.

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APPENDIX

Relationship Between Junge's Equation 1 and Yamasaki's Equation 2.

Assume that ϕ , the fraction of aerosol-bound SOC, is equal to the fraction of filter-retained SOC:

$$\text{Equation 1: } \phi = F/(A+F) = c\theta/(p^0 + c\theta)$$

$$1 + A/F = 1 + p^0/c\theta, \text{ or } A/F = p^0/c\theta$$

θ is the surface area of suspended particulate matter per cubic cm air, and is therefore $= k(\text{TSP})$:

$$A/F = p^0/ck(\text{TSP})$$

$$\text{Log } A(\text{TSP})/F = \text{Log } p^0 - \text{Log } ck$$

The temperature dependence of p^0 over the range where the heat of vaporization can be considered approximately constant is:

$$\text{Log } p^0 = m'/T + b'$$

Combining these last two equations:

$$\text{Log } A(\text{TSP})/F = m'/T + b' - \text{Log } ck$$

Setting $m = m'$ and $b = b' - \text{Log } ck$ give Equation 2:

$$\text{Log } A(\text{TSP})/F = m/T + b$$

Note that, in the case of physical adsorption, the slope (m) of Equation 2 is the same as the slope (m') of $\log p^0$ vs $1/T$.

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FIGURES

1. PCB, DDE, and HCB in an air sample from Stockholm, January, 1985. Most organochlorine pesticides have been removed by silicic acid fractionation.
Column: 25 m fused silica BP-1 bonded phase (SGE Corp.).
2. Equation 2 plots for Aroclor 1254 and alpha-HCH.
 - Columbia, SC
 - New Bedford, MA
 - ▲ Denver, CO
 - ◆ Stockholm, Sweden
3. Relationships between $A(TSP)/F$ at 20°C and p^0_L , field data. Circles and bars = organochlorines. HCB = hexachlorobenzene, HCH = alpha-hexachlorocyclohexane, CHLOR = cis- + trans-chlordane + trans-nonachlor, A. 1254 = Aroclor 1254, DDE and DDT = p,p'-DDE and p,p'-DDT. Bars for HCH and HCB span the range of $A(TSP)/F$ at 20°C obtained by extrapolating Equation 2 with regression slope m (Table 3) and slope m' for $\log p^0_L$ vs $1/T$. Filled triangles = PAH in Tokyo, ref. (73); open triangles = PAH in Columbia, ref. (71). PH = phenanthrene, FLA = fluoranthene, PY = pyrene, BkF = benzo(k)fluoranthene, BaP and BeP = benzo(a)- and benzo(e)pyrene.
4. Laboratory system for equilibrating particle-loaded GFFs with SOC vapors.
5. Changes in vapor concentration with air volume in laboratory equilibration system, monitored by PUF plugs behind GFFs (see Figure 4).
6. Apparent vapor-particle partition coefficients, $A(TSP)/F$, at different air volumes. Equilibration times ranged from about 9 h at 150 m³ to 54 h at 1360 m³.

7. and 8. Relationships between $A(TSP)/F$ at $20^{\circ}C$ and p°_S or p°_L , laboratory data.

1 = HCB, 2 = alpha-HCH, 3 = gamma-HCH, 4 = trans-chlordane,

5 = cis-chlordane, 6 = p,p'-DDE, 7 = p,p'-DDT.

9. Comparison of field and laboratory $A(TSP)/F$ at $20^{\circ}C$. Ranges of field $A(TSP)/F$ are shown for HCB and HCH assuming Equation 2 slopes m (solid circles) and m^1 (broken circles).

1 = HCB, 2 = alpha-HCH, 3 = gamma-HCH

4 = trans-chlordane, 5 = cis-chlordane

6 = sum of chlordanes (field samples)

7 = p,p'-DDE, 8 = Aroclor 1254

9 = p,p'-DDT

STOCKHOLM AIR

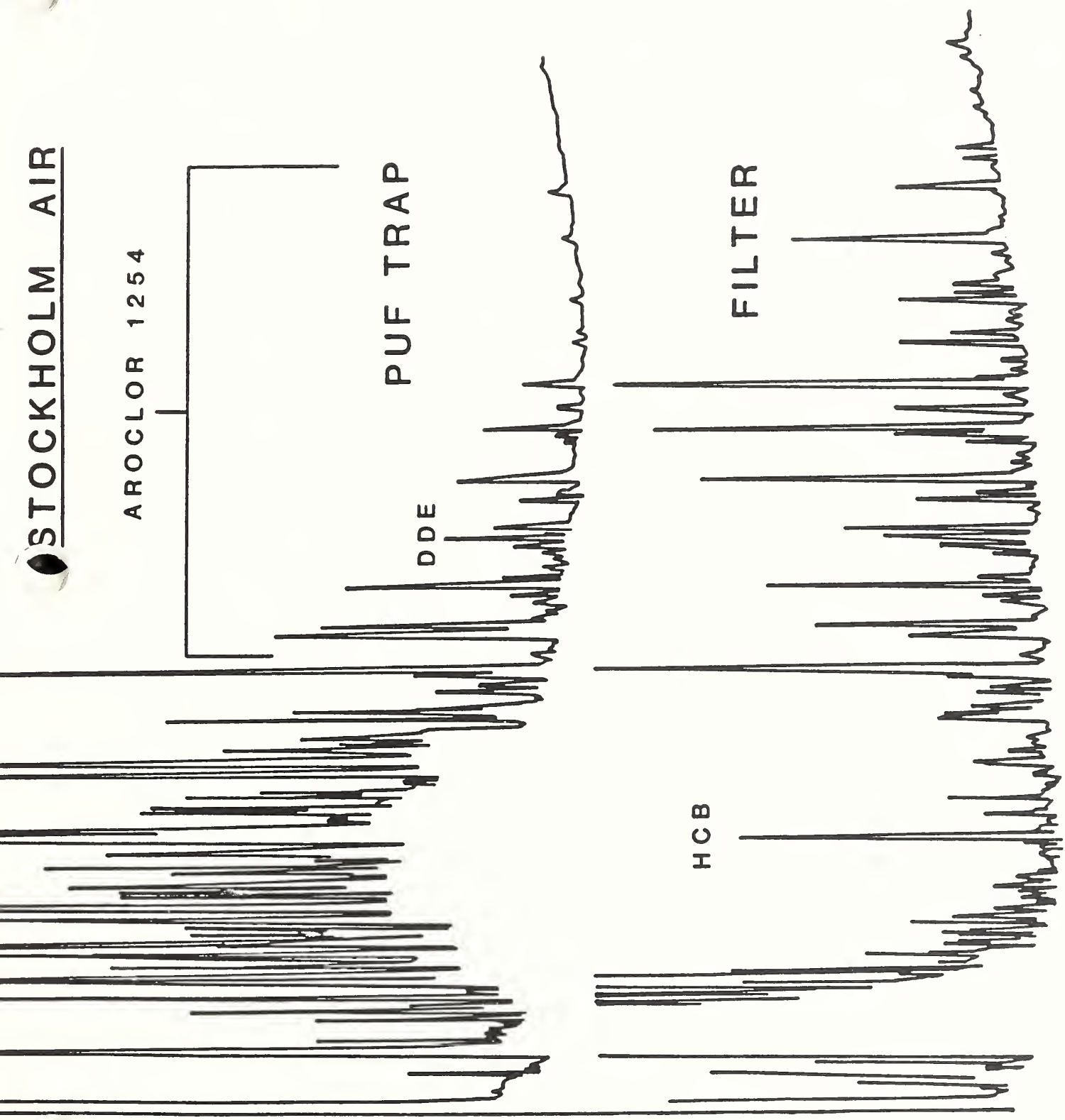
AROCLOR 1254

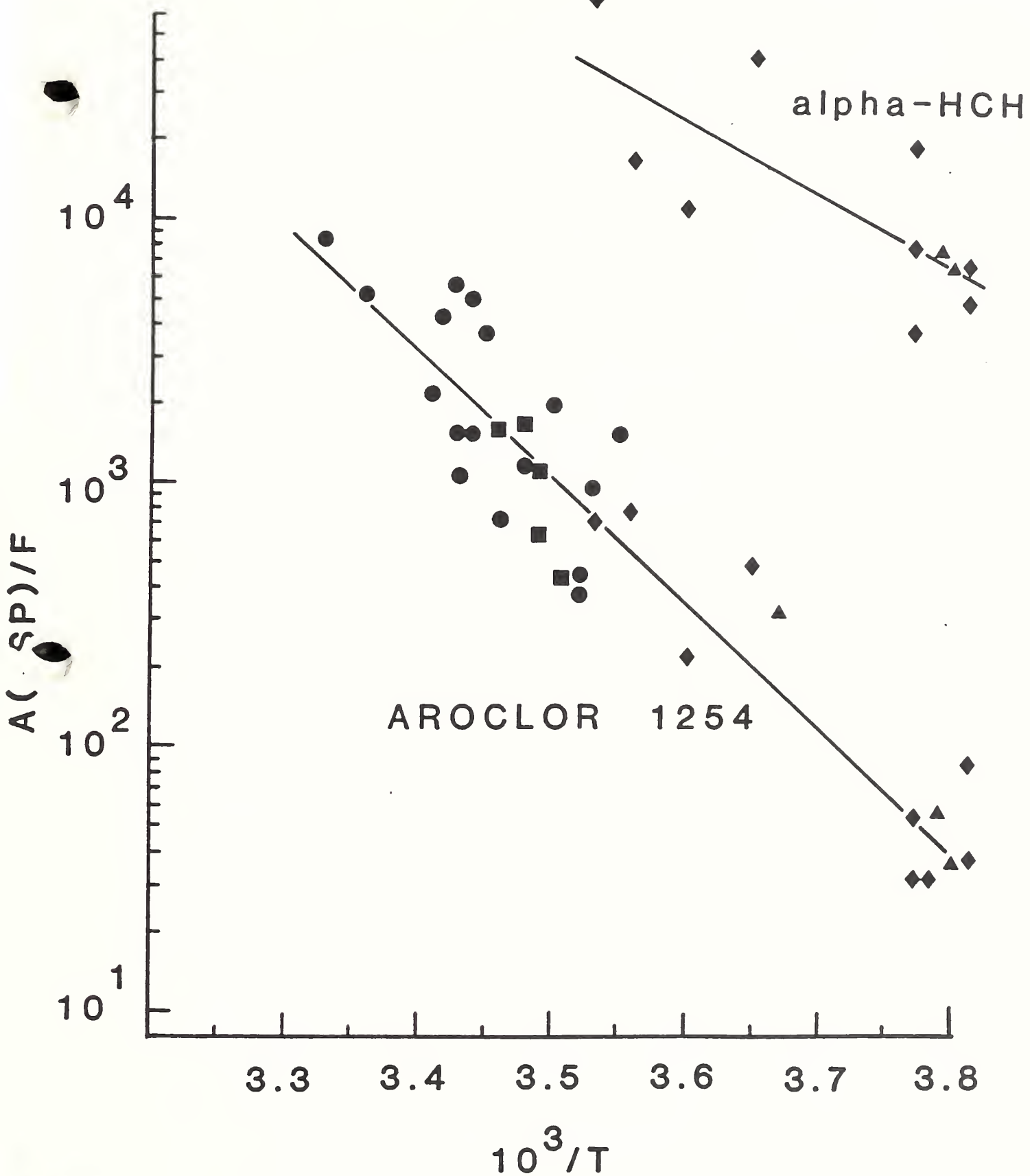
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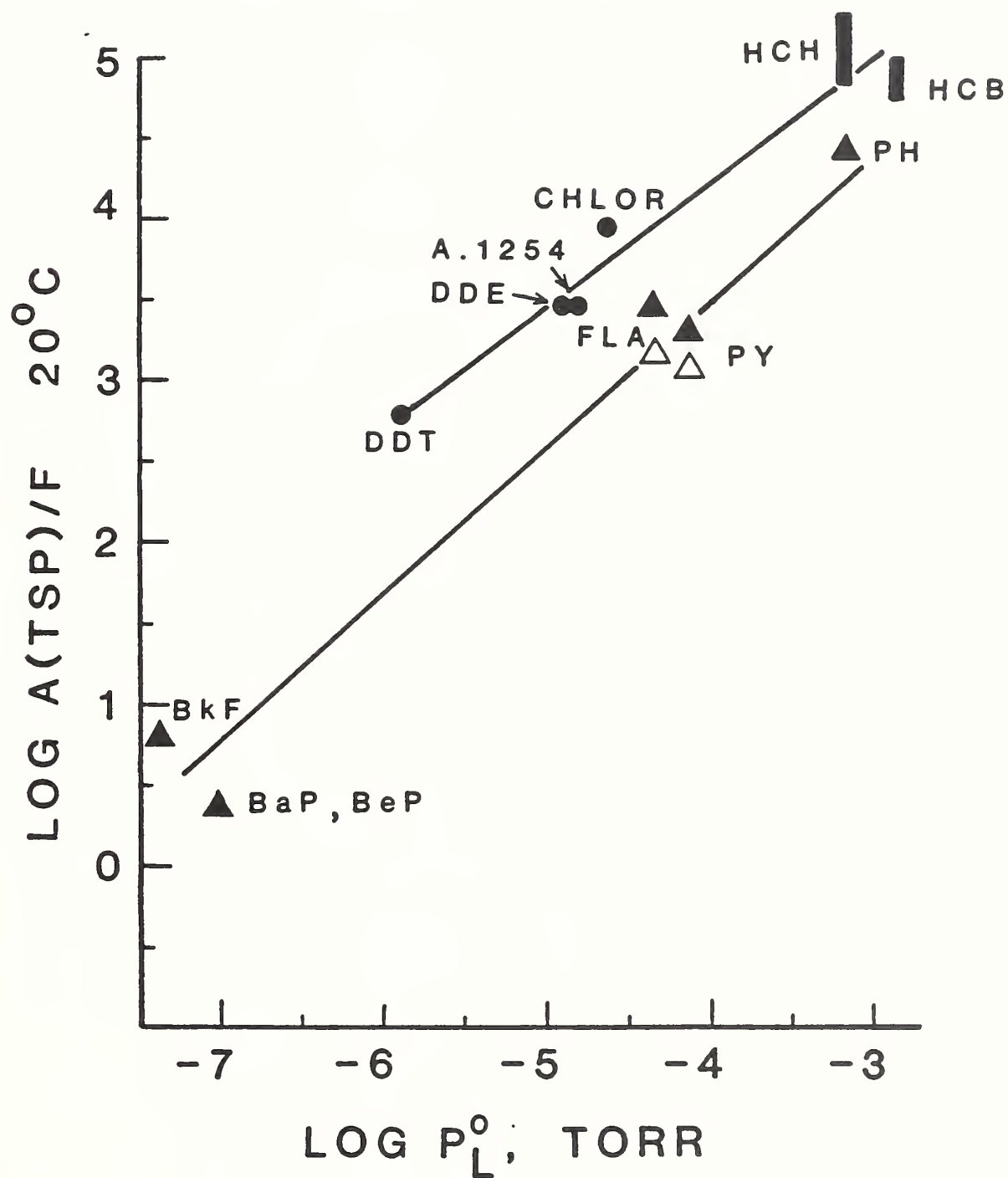
DDE

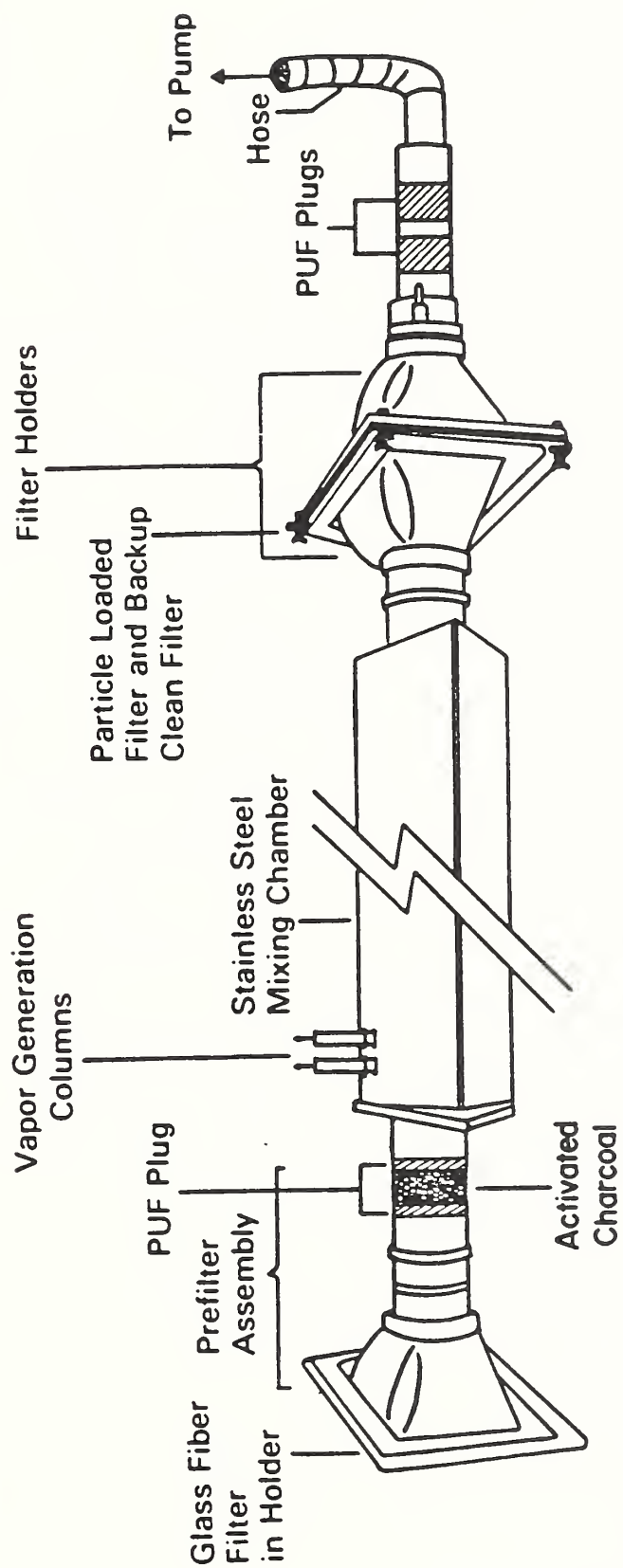
FILTER

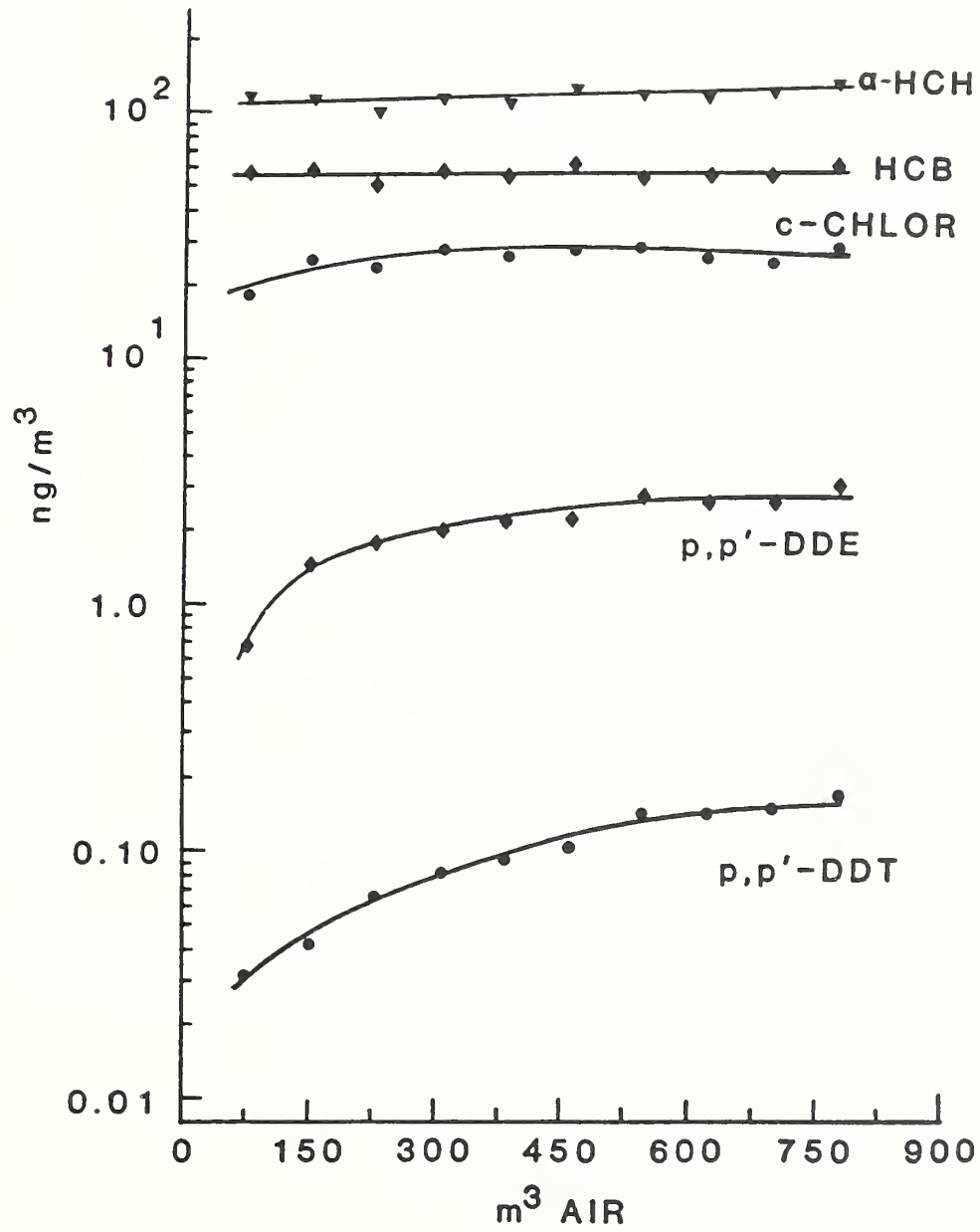
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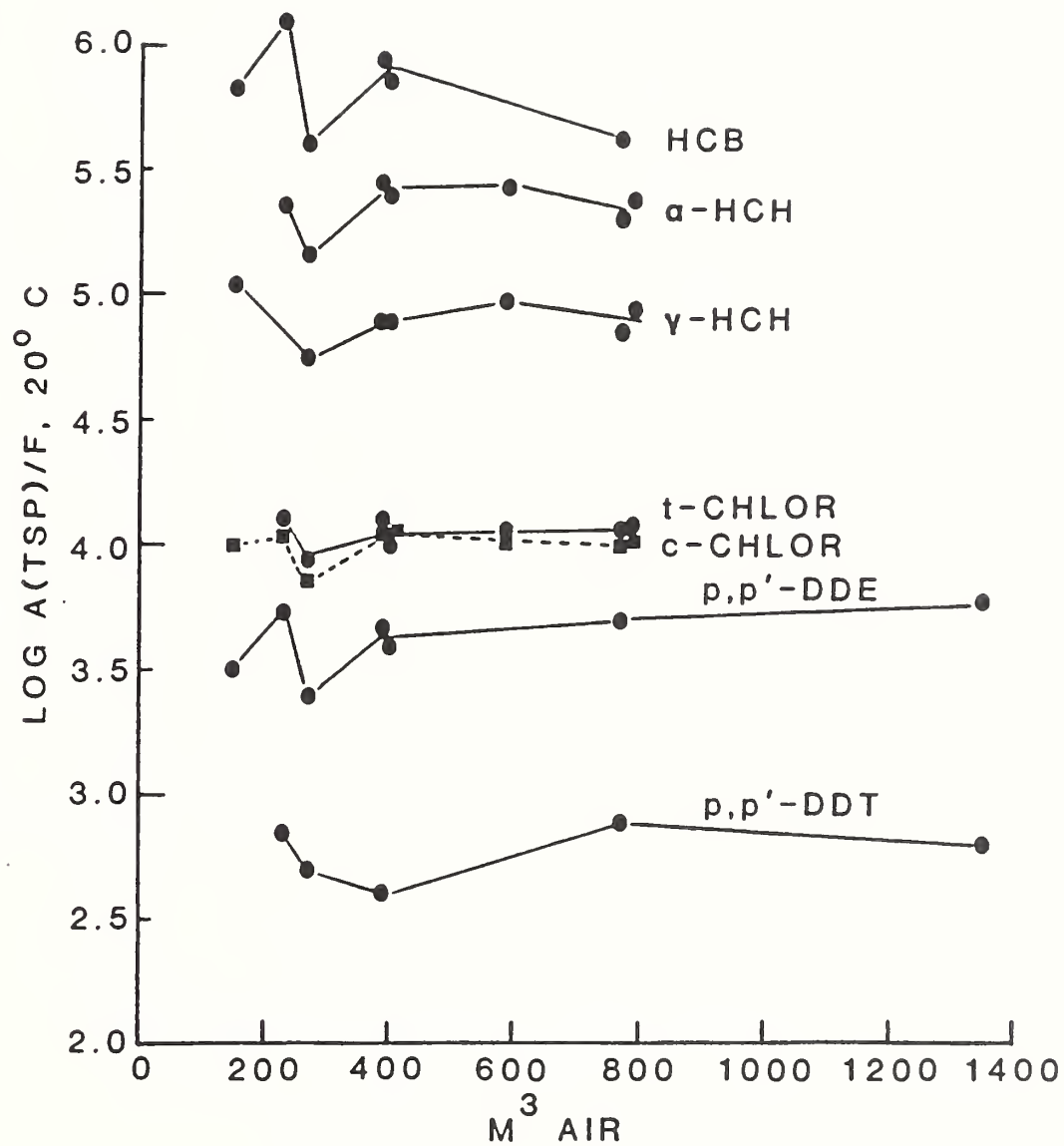


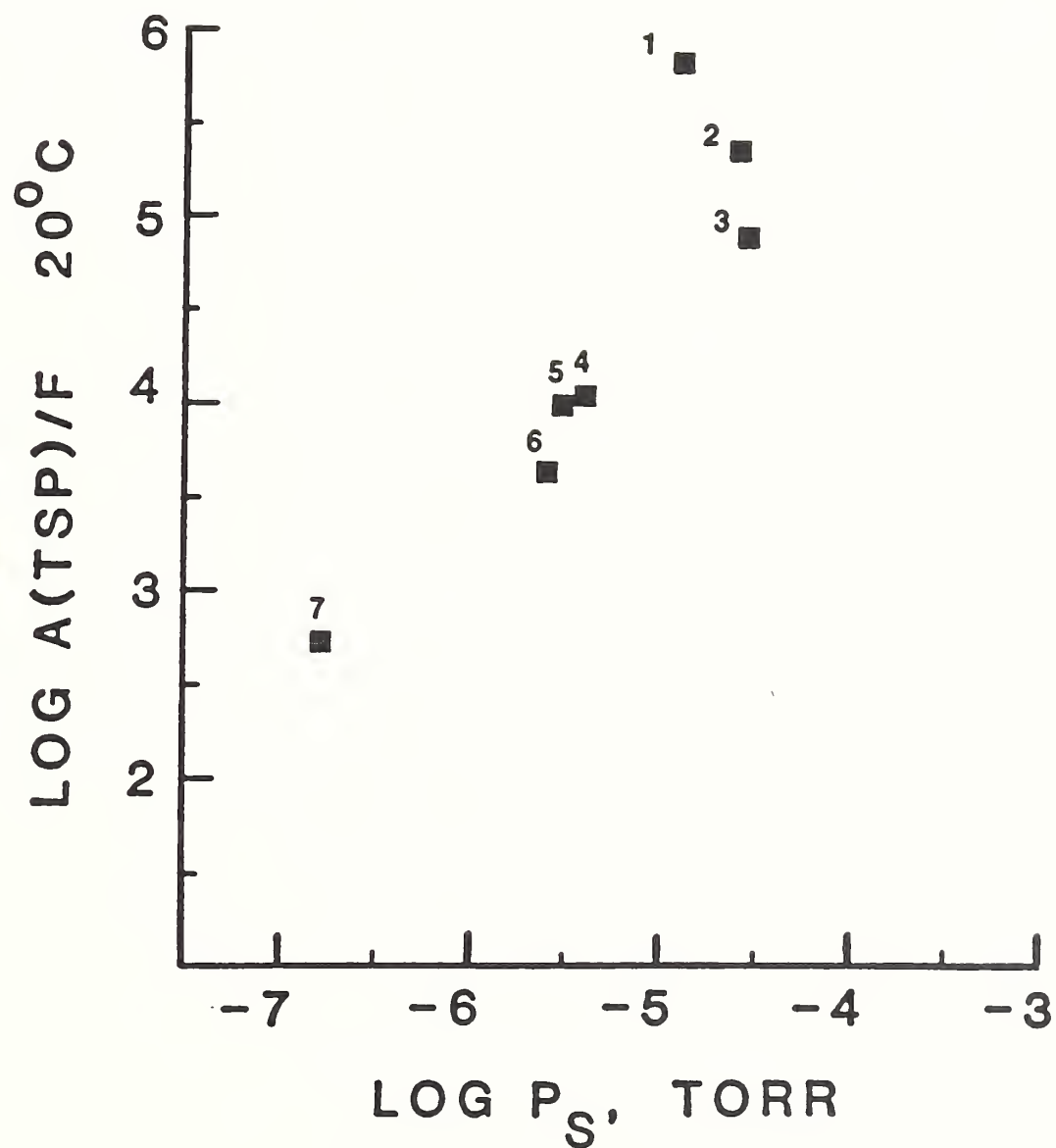


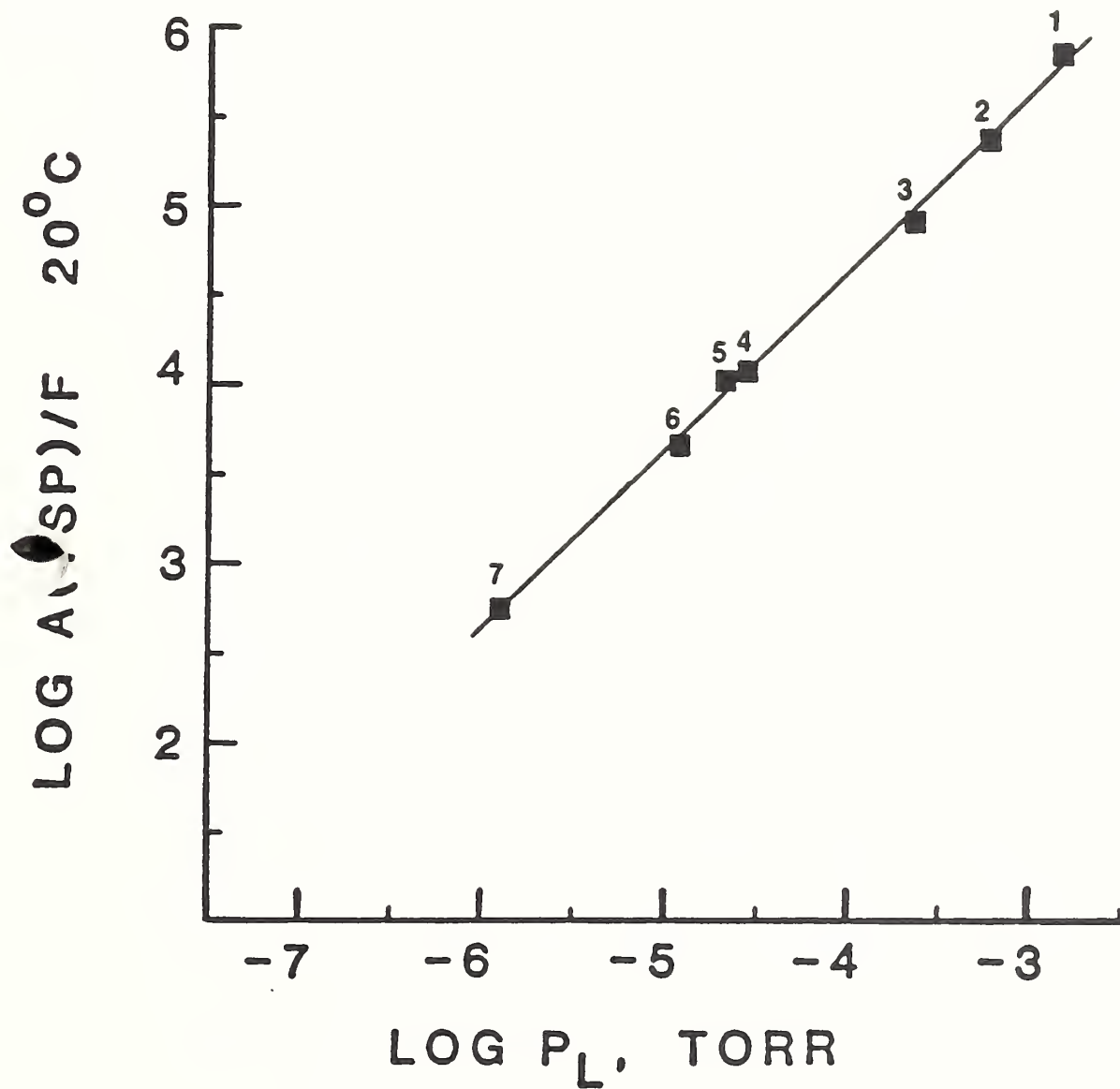


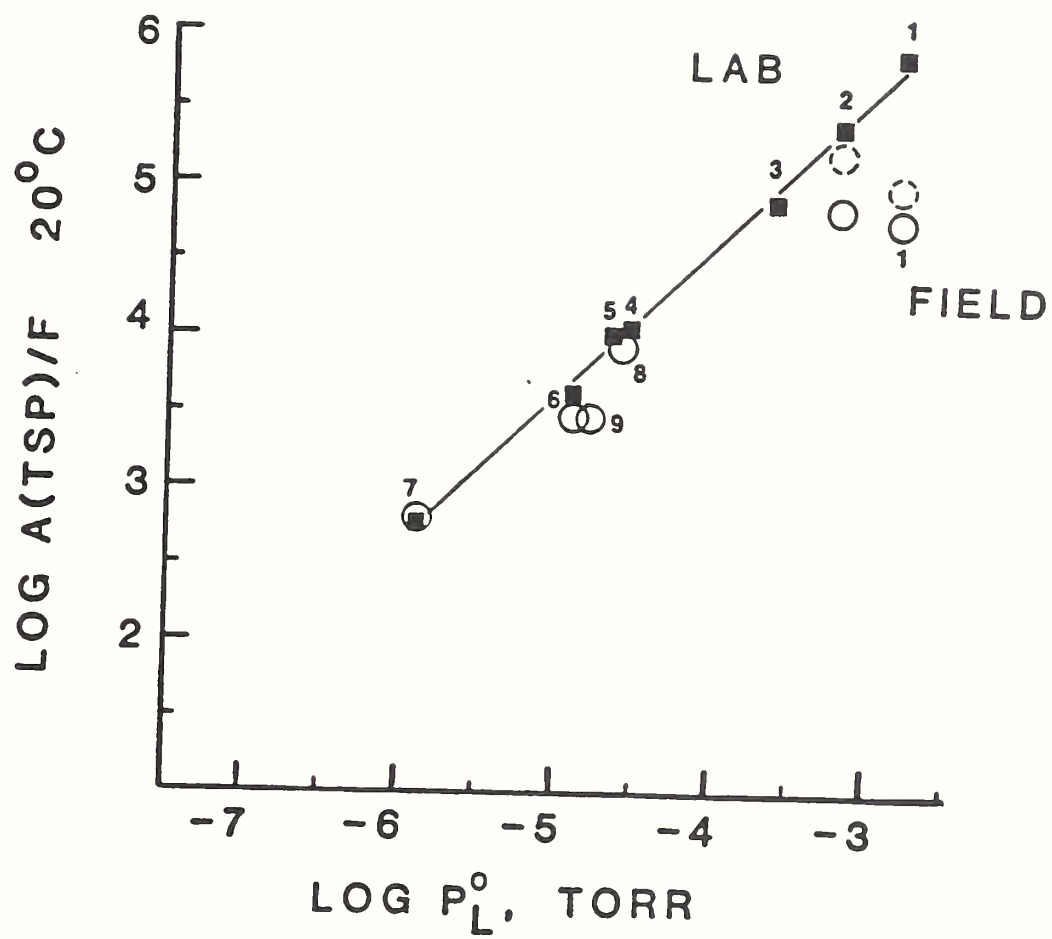












ESTIMATES OF VAPOR-PARTICLE PARTITIONING FOR
POLYCHLORINATED BIPHENYLS AND OTHER SEMIVOLATILE ORGANIC
COMPOUNDS IN DENVER AIR.

INTRODUCTION

Atmospheric residence times of trace organic pollutants depend on the chemical and physical properties of the constituents which control their removal. Removal processes include destruction mechanisms (i.e., reactions with oxidizing species or photolysis) (1-4), precipitation scavenging (5-8), dry deposition of aerosols (5,8-10), and dry gas exchange with various surfaces (e.g., air-sea exchange) (9). For semivolatile organic compounds (SOC), a critical consideration in modeling removal mechanisms is the distribution of these contaminants between the vapor and particle-associated phases.

The importance of vapor-particle (V/P) partitioning to removal processes is demonstrated by considering precipitation scavenging. Simultaneous particle and equilibrium gas scavenging has been shown by Pankow et al. (6) to be approximated by the overall washout ratio $W = (\mu\text{g}/\text{m}^3) \text{ rain} + (\mu\text{g}/\text{m}^3) \text{ air}$:

$$W = W_g(1-\phi) + W_p\phi = [RT/H](1-\phi) + W_p\phi$$

where $W_g (= RT/H)$ is the scavenging ratio for a gas, W_p is the scavenging ratio for particles, ϕ is the fraction ($0 \leq \phi \leq 1$) of compound associated with the particle phase as defined by Junge (11), H is the temperature (T) dependent Henry's Law constant (the ratio of vapor pressure to water solubility), and R is the universal gas constant. The dominance of gas or particle scavenging depends on the relative magnitudes of $W_g(1-\phi)$ and $W_p\phi$ terms (12). Dry

deposition is similarly influenced by the V/P partitioning (9,10). Adsorption to aerosols can also affect photo- and non-photochemical degradation, since many of these reactions occur only under homogeneous (gas phase) or heterogeneous (substrate adsorbed onto an aerosol) conditions (4).

Field (8,13-17) and laboratory (18) investigations of organochlorine pesticides, polycyclic aromatic hydrocarbons (PAH), and polychlorinated biphenyls (PCB) have shown that the apparent V/P distribution, estimated by the adsorbent-retained to filter-retained ratio (A/F) from high volume air sampling, is governed in large part by the vapor pressures of these non-polar SOC. However, several of these studies (16,18) indicated that there were differences in A/F partitioning for the organochlorine (OC) compounds and PAH, with the latter exhibiting an apparently greater preference for the particle phase.

This field study was undertaken to investigate further the A/F partitioning characteristics of PAH and OC, and was expanded to include n-alkanes and individual PCB congeners. Aerial concentrations of a large number of individual PCB congeners are reported here for the first time, and concentrations of total PCB obtained by summing the individual congeners are compared with total PCB calculated as Aroclor mixtures.

Denver, Colorado was selected as the air sampling location for three reasons:

1. Cold weather was desired to provide higher levels of

SOC on the filter, and thus increase detection capabilities and analytical precision, and to help reduce breakthrough of the more volatile PCB on PUF.

2. A few samples had been taken previously in Denver by our laboratory for studies of organochlorine pesticides and PCB (19).

3. Denver has a notorious atmospheric pollution problem (as exhibited by the infamous "Brown Cloud" (20)) which would ensure that sufficient amounts of the PAH would be collected in 24 hours or less.

EXPERIMENTAL

Collection of Denver Samples

Procedures for adsorbent cleanup, sample collection, and analysis have been given in detail elsewhere (14,19,21-24, Chapter 1) and will only be described briefly here.

High volume air samples were collected by pulling air at $0.35\text{--}0.5\text{ m}^3\text{ min}^{-1}$ through a 20 x 25-cm glass fiber filter followed by two 7.8-cm diameter x 7.6-cm thick polyurethane foam (PUF) plugs (density = 0.022 g cm^{-3}). The filter holder was topped with an inverted solvent-rinsed aluminum roasting pan. This simple roof (which is similar to the lid used on conventional hi-vol samplers (25)) was used to protect the filter from precipitation and direct sunlight (thereby reducing the chance of photochemical losses of PAH). The sampler was connected by 5-m of flexible hose to a Rotron DR-313 brushless pump. Flow rates were related to the pressure drop behind the sampling train by using an orifice calibrator.

Filters were precleaned by wrapping in solvent-rinsed aluminum foil and baking at 425°C for 6 h (October 1985 sample set). In an effort to reduce further filter blank levels (January 1986 sample set), filters baked under the above conditions were removed from the oven while still warm, briefly unwrapped, and then rewrapped and baked for another 6 h at 425°C. Clean filters were sealed in foil with masking tape for transportation and storage. Before and after sampling, filters were desiccated overnight over anhydrous calcium sulfate (Drierite) and weighed to obtain TSP. Filter blanks were subjected to the same transport, storage, sampler loading and analysis procedures used with actual filter samples.

PUF plugs were precleaned as previously described (21,23,24, Chapter 1), and stored and transported in individual steel cans sealed with masking tape. The second PUF plug in the sampler acted as a plug blank for all compounds except n-octadecane and the dichlorobiphenyls. For these compounds some breakthrough to the second plug was observed (5-40% of plug 1 levels) on days when sampling temperatures were >10°C.

All samples were collected 12 m above street level on the roof of a building located at 414 14th Street in downtown Denver, CO. This building is used by the Colorado Department of Health as a permanent sampling location for TSP monitoring.

Analytical Methods

Filters were cut into strips and refluxed for 24 h in dichloromethane. PUF plugs were soxhlet extracted for 24 h in petroleum ether. Extracts were then reduced to 3-5 mL on a rotary evaporator, and filter extracts were transferred to hexane during this step. All samples were then cleaned-up and separated into "nonpolar" (fraction 1) and "polar" (fraction 2) fractions using an alumina-silicic acid column chromatography procedure previously described (14, Chapter 1). Fraction 1 contained the n-alkanes, hexachlorobenzene [HCB], heptachlor, 2,2-bis(2-chlorophenyl)-1,1-dichloroethene [p,p'-DDE], and the PCB. Fraction 2 contained the PAH, α - and γ -hexachlorocyclohexane [α -HCH and γ -HCH], cis- and trans-chlordane [c-CHLOR and t-CHLOR], trans-nonachlor [t-NONA], 2,2-bis(2-chlorophenyl)-1,1,1-trichloroethane [p,p'-DDT], and toxaphene. Fractions were reduced to 2-3 mL using a stream of N₂, transferred to 10 mL centrifuge tubes, and adjusted to appropriate volumes for analysis using N₂ evaporation.

The fraction 1 samples were analyzed for "nonpolar" total extractable organics (TEO) and n-alkanes on a Carlo Erba 4160 series gas chromatograph with flame ionization detection (GC-FID) using a 25m x 0.22mm i.d. BP-1 (methyl polysiloxane) fused silica capillary column with a 0.25 μ m film thickness (SGE Inc., Austin, TX). Analysis conditions were: splitless injection (1-2.5 μ L, 30 seconds), 250°C injector temperature, FID at 320°C, 1.2 mL/min He carrier gas flow, split flow 80 mL/min, temperature program - inject

at 80°C, then programmed at 5°C/min to 300°C.

PAH in fraction 2 were analyzed using reverse-phase high performance liquid chromatography (HPLC) with fluorescence detection. The HPLC system and conditions were the same as that previously described (14,18, Chapters 1 and 3). The PAH were separated on a 25-cm x 4.6-mm i.d. Vydac 201TP104 10 μ m C-18 column (The Separations Group, Hesperia, CA) using the solvent program: initial 55% CH₃CN-H₂O, increasing at 2.4% CH₃CN min⁻¹ to a final 95% CH₃CN-H₂O mixture.

For one Denver sample (D7) selected HPLC peaks from the filter and plug were collected and analyzed by GC with mass spectroscopic detection (GC-MS) in the electron impact mode to assist in peak identification. The GC-MS was a Finnigan 4521C instrument fitted with a 25 m x 0.20mm i.d. SE-54 (5% phenyl methyl polysiloxane) fused silica capillary column with a 0.33 μ m film thickness (Hewlett-Packard, Avondale, PA). Other analysis conditions were: splitless injection at 60°C (1 μ L, 30 seconds) then increased at 20°C/min to 180°C, then increased at 5°C/min to 300°C; MS scanning from 100 to 350 amu in 1 s.

Fraction 1 and 2 organochlorines were determined by GC-ECD after shaking extracts with concentrated H₂SO₄. Analyses were conducted on a Varian 3700 instrument using splitless injection (1-2.5 μ L, 30 seconds). The temperature program was initially 90°C, then increased at 4°C min⁻¹ to 295°C. Separations were carried out on a 25 m x 0.20 mm i.d. SE-54 fused silica capillary column with a 0.33 μ m film

thickness (Hewlett-Packard, Avondale, PA). Other analysis conditions were: H₂ carrier gas 1.8 mL min⁻¹, split flow 80 mL min⁻¹, injector and detector temperatures 240° and 320°C, respectively.

Chromatographic data were collected in the peak area mode using a Hewlett-Packard 3390A or a Shimadzu Chromatopac C-R3A integrator. Injection standards were prepared in-house using n-alkanes and PAH obtained from the Foxboro Company, New Haven, CT; Aroclor fluids (PCB) from Monsanto Corp., St. Louis, MO; and organochlorine pesticides from the EPA Pesticides and Industrial Chemicals Repository, Research Triangle Park, NC.

Known quantities of n-alkanes, PAH, organochlorine pesticides and PCB injection standards were spiked in combination onto three PUF plugs, and carried through the entire analytical procedure in a recovery study.

RESULTS AND DISCUSSION

Analytical Recoveries

Many trace contaminant analysis techniques rely on preconcentration methods for collection of enough material for detection. In addition, one or more cleanup steps is usually necessary to remove interfering compounds before final quantitative analysis. Spike-recovery studies are necessary to evaluate losses during the extraction and cleanup procedures.

Previous investigations have shown that petroleum ether extraction gives good recoveries of n-alkanes, PAH and chlorinated hydrocarbons from PUF and provides acceptable

blank quantities (14,26). A number of solvents are routinely used for the extraction of PAH from particulate matter, with benzene, toluene, dichloromethane, or solvent mixtures containing one of these solvents generally performing well (27-30). Our laboratory routinely uses dichloromethane because of reported good extraction efficiencies for PAH (27), and its volatility, which enhances easy exchange to hexane before column cleanup and analysis by GC-ECD and HPLC.

Field samples are mixtures of numerous classes of compounds and the spike-recovery study was designed to simulate the multicomponent nature of real samples, at least with respect to the compound classes of interest here. Combinations of injection standards were spiked onto PUF and carried through the entire analytical procedure, including a final volume reduction step using N_2 evaporation to 400-500 μ L for the non-polar fraction and 200 μ L for the polar fraction.

Spike-recovery data for the four categories of compounds undergoing investigation are presented in Tables I-IV. Table I reveals that recoveries of n-alkanes from eicosane to tetracosane were complete, with octadecane exhibiting an average 78% recovery. Recoveries for lighter alkanes were lower due to volatilization losses. Sampling temperatures in Denver averaged $\leq 12^\circ\text{C}$, providing complete collection on 2 PUF plugs of organic material having vapor pressures less than or equal to octadecane. This allowed for quantification of octadecane in the samples, which was

useful in calculating hydrocarbon preference indices (see below).

Previous field investigations of component breakthrough on PUF plugs indicated that collection of hydrocarbons \geq nonadecane (C-19) was complete under most sampling situations (14, Chapter 1). In the past our laboratory routinely used this C-19 cut-off for determinations of total extractable organic (TEO) concentrations, and this cut-off was retained here for comparison purposes.

Organochlorine (OC) recoveries are presented in Table II. PCB (Aroclor fluids) and DDE are found in the non-polar fraction, and show rather low but consistent recoveries (55-65%). HCB and heptachlor are also contained in this fraction. However, their recoveries were $<40\%$ and therefore, they were not considered in this study. The chlordanes, trans-nonachlor, p,p'-DDT and the toxaphene components are contained in the polar fraction. With the exception of DDT and toxaphene, the recoveries of these OC were also lower than the $>80\%$ level desired. Recoveries of α - and γ -HCH, which elute in the polar fraction, were less than 40%. These pesticides were also omitted from this study for this reason. Losses of the OC were lower than anticipated based on their vapor pressures (Table XVIII) and the alkane recoveries. In fact, the liquid phase vapor pressure of γ -HCH at 20°C (2.5×10^{-4}) is only 2.2 times higher than n-octadecane (1.1×10^{-4}). Losses of the OC were believed to be due mostly to the additional N_2 evaporation step performed during clean-up with concentrated

H₂SO₄, a necessary step before GC-ECD analysis.

DDE coelutes with a PCB congener and the chlordanes, trans-nonachlor, and DDT coelute with toxaphene peaks. As a result it was necessary to use a subtraction technique to correct for contributions of PCB or toxaphenes to the pesticide peak areas. This technique generally must be used for real samples, and the spike-recovery study was designed to simulate this difficult analytical problem. The overall contribution of this subtraction method to the low recoveries is unclear, but the very good DDT recovery and the poor recoveries of other compounds (HCB, HCH, heptachlor) free from coeluting PCB or toxaphene congeners suggests that this correction method was not largely responsible for the low recoveries. Since the more volatile OC exhibited poorer recoveries, it must be inferred that volatilization losses during the various solvent reduction steps contributed the most to the low recoveries. Constable et al. (31) compared several solvent reduction methods and have shown slightly lower recoveries of the PAH fluorene using N₂ evaporation with methylene chloride (63%), than with pentane (87%) or acetone (84%), also suggesting volatility losses for the organochlorines.

PAH analytical recoveries are shown in Table III. In general the recoveries were acceptable, with PH and AN showing slightly lower recoveries due to their greater volatilities. The recovery of non-volatile coronene was also low. Possible reasons for the lower coronene recovery include partial extraction from PUF using petroleum ether,

incomplete elution from the alumina-silicic acid column, or adsorption to the centrifuge tube glass walls due to its low solubility in hexane (or isooctane).

National Bureau of Standards urban dust standard SRM-1649 (collected in Washington, DC, lot date April 1982) was analyzed as an additional check on the analytical procedure for PAH. Triplicate dust samples approximately 200 mg each were placed in pre-baked ceramic thimbles and extracted for 24 h with dichloromethane, followed by sample clean-up, fractionation, and quantification as described above for filter samples. Results of the SRM-1649 recoveries in June 1986 and from an earlier recovery check in September 1984 are presented in Table IV. Certified concentrations are available for fluoranthene [FLA], benzo(a)pyrene [B(a)P], benzo(ghi)perylene [B(ghi)P], and indeno(1,2,3-cd)pyrene [INDENO], with uncertified concentrations given for the other PAH in Table IV (30,32,33). Levels of phenanthrene [PH] in SRM-1649 were too low to allow for accurate determination using our HPLC system.

Recoveries of FLA, benzo(k)fluoranthene [B(k)F], and B(ghi)P, corrected for procedural losses, were within the acceptable recovery range and were greater than those determined in September 1984. Dibenz(ah)anthracene [Di(ah)AN] was found to coelute with B(ghi)P from sample spiking studies. Bartle et al. (29) published HPLC chromatograms of PAH standards on a Vydac TP-201 column, showing Di(ah)AN and B(ghi)P separated. However, published PAH retention indices from SRM-1649 separated on a Vydac TP-

201 column suggests that coelution of these two PAH on our HPLC system was likely (30,32). Reported concentrations of Di(ah)AN in SRM-1649 were only 10% of B(ghi)P concentrations (30,32), and correction for procedural losses using B(ghi)P probably does not mis-represent the combined concentrations of these two PAH. GC-MS analysis of the peak containing B(ghi)P in the D7 Denver filter sample (see section on "PAH in Denver Air" and Table XI) did not reveal the presence of Di(ah)AN at the limit of detection. As a result the fluorescence contribution of Di(ah)AN to the peak identified as B(ghi)P was probably small.

The recovery of INDENO in SRM-1649 was 200%, strongly suggesting a coeluting peak(s). GC-MS analysis of the fractionated INDENO peak from HPLC analysis of Denver sample D7 (Table XI) revealed an unknown compound with base m/e of 276. The unknown component concentration was approximately 15% of the INDENO concentration by GC-MS, however this unknown peak may fluoresce strongly in the wavelength region isolated by our fluorimeter, resulting in a greater contribution to the total fluorescence. The concentration of INDENO would thus be over represented, and consequently all INDENO concentrations reported for the Denver samples are not corrected for procedural losses and are upper limits.

Recovery of pyrene (PY) from SRM-1649 was below the desired $\geq 80\%$ and was also lower than observed during a previous analysis in September 1984. Far worse was the recovery of benzo(a)pyrene [B(a)P], which was quite

surprising in light of the good recovery (average = 85%) from the PUF plug spike recovery study. The low B(a)P recovery was of particular concern due to the importance of this carcinogenic PAH (34). Previous air samples analyzed in our laboratory contained B(a)P, confirmed by fluorescence spectroscopy and GC-MS (14). Additionally, the September 1984 analysis of SRM-1649 revealed a peak identified as B(a)P (with 69% corrected recovery) from pattern matching with earlier Columbia (14) and SRP (Chapter 1) air samples. The reason for the low B(a)P recovery in June 1986 is unclear, but it is probably not related to the age of the SRM-1649 material, which was stored in a brown bottle at room temperature in the dark for approximately two years. NBS reported good recoveries of B(a)P from SRM-1649 stored under similar conditions since 1982 (35). GC-MS analysis of the Denver D7 sample fractionated HPLC peak suspected to contain B(a)P revealed no B(a)P at the limit of detection. However, subsequent recovery checks on a B(a)P standard indicated that isolation of B(a)P from the HPLC mobile phase solvent was probably incomplete (see "PAH in Denver Air" section). However, this still does not explain the poor recoveries of B(a)P from SRM-1649.

A number of studies have shown that selected PAH can undergo both photo-induced and non-photochemical degradation reactions (36-47). The majority of these were laboratory or field investigations in which PAH adsorbed on various supports (alumina, silica, fly ash, soot, diesel particles and airborne particles collected on filters) were exposed

under various conditions to O_3 , NO_x , SO_x , and strong acids. Most of these studies have revealed that portions of exposed PAH, including PY and B(a)P, can be transformed into a variety of products, including nitro- and oxygenated PAH (36-40,44-47). More recently, field investigations assessing the importance of PAH degradation have confirmed the degradation of PAH in the ambient atmosphere and the presence of some of these degradation products (41-43,45,48-50). These findings are of tremendous significance to the collection of PAH in the air, and may also be relevant to possible degradations during sample work-up and analysis.

Ligocki and Pankow (51) reported good recoveries for anthracene- d_{10} , fluorene, and pyrene (102, 85, and 103%, respectively), but only a mediocre recovery of $64 \pm 22\%$ for B(a)P, using an extraction and florisil cleanup-fractionation procedure (pentane-dichloromethane eluate) that is similar to the procedure used here. Though they gave no reason for this low recovery relative to the more volatile PAH, degradation of B(a)P during column cleanup may have been the cause. Indeed, a number of other investigators have reported the photo- and non-photochemically induced reactivity of B(a)P and other PAH adsorbed on alumina (52-57) and silica (57). More recently, Yokely et al. (58) investigated the photochemical transformation of PY and B(a)P vapor-deposited on eight coal stack ashes, alumina, and silica gel. They found $\geq 60\%$ degradation of both PAH after 24 hour exposures to UV radiation on alumina, silica gel, and controlled-pore glass.

Appreciable degradation of these PAH was observed on only two of the eight fly ashes, and at a lower percentage than that seen with the non-ash adsorbents. They found no detectable photochemical degradation on ash containing greater than 0.5% carbon or 10% iron, and suggested that this might be due to an inner filter suppression of adsorbed PAH photolysis by the highly colored, porous ash substrates.

In light of the above findings, concentrations of B(a)P reported for Denver samples are probably lower limits, and based on B(a)P recoveries from SRM-1649, actual concentrations of B(a)P may be approximately 2-8 times higher. Certainly, additional studies of PAH degradation during column cleanup and air sampling are warranted to help further define these degradation and/or loss processes.

Collection of Denver Samples

Denver collection and TSP concentration data are presented in Table V. Four samples were collected in October 1985, and five in January 1986. Except for samples D1, D3, and D4, the temperature fluctuation over the sampling period was less than 10°C for all samples, and was less than 5° for four of them. Smaller fluctuations were the result of sampling only during the day or night, reducing the effects of diurnal variations.

Hazy, polluted conditions occurred on days with TSP concentrations above 80 $\mu\text{g}/\text{m}^3$. The mean TSP concentration was 84 $\mu\text{g}/\text{m}^3$ for both sampling periods, and ranged from a low of 27 $\mu\text{g}/\text{m}^3$ on January 6-7, 1986 (D5) to a high of 157

$\mu\text{g}/\text{m}^3$ just 24 h later. This shows the dynamic nature in which climatic and/or emission changes can dramatically affect the atmospheric burden. TSP concentrations observed during the January 1986 period averaged $105 \mu\text{g}/\text{m}^3$. Billings and Bidleman (19) reported Denver TSP concentrations in January 1980 ranging from $117\text{--}157 \mu\text{g}/\text{m}^3$. Shah et al. (59) reported a 1975 annual average TSP in Denver of $108 \mu\text{g}/\text{m}^3$. Countess et al. (20) reported a mean TSP concentration in Denver of $104 \mu\text{g}/\text{m}^3$ and range of $25\text{--}216 \mu\text{g}/\text{m}^3$ for November-December 1978. These literature values show that the TSP observed in this study were comparable, and that the particle load during the winter in Denver is still high.

Comparison of Filter Blank Levels

Table VI compares quantities of contaminants found on filter blanks from the fall and winter sampling periods. For the second sampling trip the two filter blanks (Blanks B and C) were double-baked at 425°C , as described in the EXPERIMENTAL section, in an effort to further reduce the contaminants. These two filter blanks were very similar. Filter blanks from fall and winter revealed no PAH contaminants above the detection limit chromatographing in the region of interest (see Figure 15). Blanks from both periods also showed little TEO contamination (see Figures 2 and 4). However quantities of DDE and particularly the lighter PCB were higher on Blank A than observed with the double-baked filters (Figure 1). Blank A quantities were substantially higher in the Aroclor 1242 region of the PCB pattern than those observed on Blanks B and C, and were

sometimes above quantities observed in real filter samples as shown in Table VI. As a result, no partitioning calculations were performed on any samples in the Aroclor 1242 region, and most of the reported concentrations of individual PCB in the Aroclor 1242 region do not include the filter. Contaminants in the Aroclor 1254 region were only slightly higher for Blank A compared to Blanks B and C, and were much lower than in the Aroclor 1242 region allowing for good quantification of 1254 region PCB. Unfortunately, the Blank A fraction 2 was lost after PAH analysis but before pesticide analysis. Therefore a comparison of fall and winter blank quantities for the chlordanes, DDT, and toxaphene was not possible.

The above results reveal distinctly less OC contamination on the double-baked filters, and suggest that additional baking might provide even lower blanks. However, baking GFF filters at higher temperatures is not recommended, since the filters tend to become brittle. Pre-extraction with chromatographic quality solvents (like dichloromethane) before baking might also reduce filter blanks.

Blank corrections were made by subtracting the amount found on the filter blank from quantities measured on the filter samples for a particular sample set. The average January filter blanks were used as a correction for the fraction 2 organochlorines in the October samples.

Total Extractable Organics and n-Alkanes in Denver Air

Three representative GC-FID chromatograms of the non-polar fraction from Denver air are shown in Figures 2-4. The chromatograms show a large unresolved complex mixture (UCM) with n-alkanes superimposed on the UCM. These figures also reveal that the sampling train was acting like a chromatograph, separating the components on the basis of their volatilities, as observed in other investigations (14, Chapter 1). Increased quantities of less volatile components were observed on the PUF plugs on warmer days (cf. Figures 2 and 4).

These chromatograms were obtained using capillary columns, which provided much more detail and allowed the quantification of individual n-alkanes from C-18 to C-32 (Table VII). In addition, TEO \geq C-19 were also quantified in the non-polar fraction as described previously (14, Chapter 1). As expected, concentrations of individual n-alkanes and TEO are generally higher on dirtier (high TSP) days. Except for D5, all Denver samples had fraction 1 TEO concentrations greater than the mean fraction 1 TEO concentration measured in Columbia, SC ($0.641 \mu\text{g}/\text{m}^3$) (14).

Average concentrations of individual alkanes associated almost exclusively with particles (C-24 to C-32), as well as those showing a partial vapor phase component (C-20 to C-23), were within a factor of two of those determined using both low and high volume particle collectors on January 9, 10, and 12, 1985 by Greaves et al. (60) in Boulder, CO, approximately 40 km northwest of downtown Denver (Table

VIII). However, average concentrations of the lighter n-alkanes (C-18 to C-19) were substantially higher (approximately 7.5 times) than those reported by Greaves et al. This is due to the greater proportions of these two alkanes in the vapor phase.

A comparison of the n-alkane fingerprints for the Denver samples provided qualitative information on the sources of hydrocarbons. All Denver samples exhibited a UCM, which was indicative of anthropogenic contributions (61), and they were similar to UCM observed by a number of other investigators (61-65). Another indicator of contamination from petroleum sources was shown by the presence of pristane and phytane in all the samples (Figures 2-4) (63). These compounds are reported to be diagenetic products of phytol and thus, are not primary constituents of most terrestrial organisms (66,67).

Relative contributions of biogenic versus anthropogenic sources are also characterized by the odd/even n-alkane ratio. A quantitative measure of this ratio is provided by the hydrocarbon (or carbon) preference index (HPI or CPI) defined as (68):

$$\text{HPI} = 1/2 \left[\frac{\sum_{i=1}^z n_o}{\sum_{i=1}^{z-1} n_e} + \frac{\sum_{i=1}^z n_o}{\sum_{i=1}^{z+1} n_e} \right] \quad (\text{Equation 1})$$

where the n_o are the concentrations of n-alkanes with odd carbon numbers from i to z, and n_e the concentrations of

those with even C-numbers. In this study the HPI was calculated using C-19 to C-31 odd n-alkanes in the numerator, and C-18 to C-30 and C-20 to C-32 even n-alkanes in the denominator.

HPI are shown in Table VII. For samples D6 and D8 there was some difficulty in quantifying at least one of the alkanes, and for these no HPI are given. HPI were calculated using the amounts found in the vapor + particle phases and in the particle phase alone. The D1 sample had a HPI value above 1.5, a level usually considered indicative of a substantial biogenic contribution (63), and indeed this sample was taken on a very clear day, with strong winds from the west. These climatic conditions have been shown by Greaves et al. (69) to result in an influx of biogenically derived material to the Denver area from the forested areas to the west. The other Denver samples showed HPI nearer to 1.0 again suggesting a predominantly petroleum-derived source.

Also of interest were the differences obtained by calculating the HPI using concentrations from the particle phase alone and from the combined gas and particle phases. The D1 sample had a large particulate HPI (2.7), but the HPI was reduced to 1.7 when the gas phase was also included. This shows that an over-estimation of the biogenic contribution to the total atmospheric burden can be interpreted using a particle-derived HPI only. Differences between HPI for the other samples calculated using the two methods were not as great since the odd-to-even ratio in the

gas and particle phases exhibited no predominance (anthropogenic).

The D1 sample (Figure 2) shows a predominance of odd-to-even n-alkanes both on the filter and in the first plug. Simoniet et al. (63) has shown that distributions of the type exhibited in Figure 2 are representative of alkanes derived from vegetation. In contrast, Figures 3 (D4) and 4 (D7) show no strong odd-to-even preference in either the filter or plugs suggestive of a larger petroleum contribution. A sizable portion of the anthropogenic hydrocarbon burden in Denver air was likely due to combustion of wood for domestic heating, and not just petroleum sources, since wood-burning fireplaces and stoves were widely used throughout the Denver area during these two sampling periods.

Organochlorine Pesticides in Denver Air

Concentrations of organochlorine pesticides are presented in Table IX. A GC-ECD chromatogram representative of the polar fraction organochlorines in Denver air from the filter and PUF plugs is shown in Figure 5, along with a toxaphene standard. Figure 6 shows a polar fraction filter blank and a pesticide standard. Concentrations of toxaphene in Denver air were so low that identification and quantification by GC-ECD was difficult. The upper limit average concentration of toxaphene in Denver air was $0.089 \pm 0.051 \text{ ng/m}^3$ by GC-ECD, compared to Columbia with an average concentration of 13.1 ng/m^3 reported from 1977-79 (19) and

$1.1 \pm 0.6 \text{ ng/m}^3$ for three samples collected in 1984-85 (18).

For two Denver samples (D4 and D9), identification of toxaphene components with six to nine chlorines was confirmed using GC with negative chemical ionization mass spectroscopic detection (GC-NCIMS) (Figures 7a-c). Details for identifying toxaphene by GC-NCIMS are given in (70). Quantification of these components by GC-NCIMS gave concentrations of 0.049 and 0.037 ng/m^3 for D4 and D9, respectively, which were only 37% and 22% of the concentrations estimated by GC-ECD. These differences are likely due to an overestimation by GC-ECD caused by electron capturing compounds underlying toxaphene peaks (a situation similar to that encountered for samples taken in Sweden (15)). Therefore, the toxaphene concentrations given in Table IX are upper limits.

The average concentration of p,p'-DDT (0.018 ng/m^3) in Denver air for the Jan. 1986 sampling period was lower than found (0.043 ng/m^3) in Jan. 1980 (15). However, average p,p'-DDE concentrations were similar. Billings and Bidleman (19) reported an average trans- + cis-chlordane + trans-nonachlor concentration of 0.063 ng/m^3 for Jan. 1980 Denver air, which was comparable to the average summed chlordanes concentration (0.073 ng/m^3) obtained in Jan. 1986.

PCB in Denver Air

Previous quantifications of PCB in our laboratory were performed by matching chromatograms with those of Aroclor fluids (15,18,19,21,23,24). In this method, the sum of all identified PCB peak areas within a particular Aroclor

retention time window is quantified against a response factor derived from the sum of Aroclor standard peak areas. For comparison purposes, this quantification technique (Method 1) was also used here.

Concentrations of individual PCB congeners were desired for calculations of A/F partitioning. Capel et al. (71) recently published chromatograms of Aroclors 1242, 1254, and 1260, identifying a large number of the fluid peaks. In addition, they reported compositional information for each Aroclor. Capel et al. noted that complete resolution of all congeners in an Aroclor was not possible, and that some GC peaks contain two or more congeners. They classified GC peaks into four groups:

1. Peaks containing only one PCB (the largest group).
2. Peaks which have two congeners with one being dominant (>90%), and noted as only a single congener.
3. Peaks which have more than one major congener (both >10%), with the dominant one noted by a * in Tables X and XI.
4. Peaks which contain more than one congener, but could not be further elucidated.

The same GC column used by Capel et al. was used in this investigation, and although different temperature programming conditions were used, the Aroclor chromatograms looked remarkably similar (Figures 8 and 9). Individual PCB congeners in Denver samples were identified by matching retention times with those in the Aroclor fluids.

Quantification of individual PCB was accomplished by deriving response factors for each congener using the average compositional information of Capel et al. (71) and Mullin et al. (72) (Method 2). Only those peaks showing no apparent interference from non-PCB peaks were used.

Figure 8 shows a GC-ECD chromatogram of Aroclor 1242 and Figure 9 a chromatogram of a mixed standard containing Aroclors 1242 and 1254. The peaks listed for the Aroclor 1242 standard were those used for identification and quantification in the 1242 region of the Denver samples, and similarly for the 1254 region. Note that not all of the Aroclor peaks were identified by Capel et al. Figure 10 shows chromatograms of the non-polar fraction filter and front plug from sample D8. Figure 11 presents chromatograms of the D8 backup plug and filter blank C. Few PCB heavier than the dichlorobiphenyls were detected on backup plugs under the cold sampling conditions. As expected, higher quantities of the less volatile PCB were found on the filters compared to the plugs. Conversely, quantities of lighter PCB on filters were often below the detection limit or blank levels. Figure 12 compares an Aroclor 1016-1254 mixed standard with plug 1 from D4 (an October 1985 sample), and Figure 13 shows chromatograms of the filter and PUF plugs from this sample. PCB chromatograms from January and October samples were qualitatively similar.

Tables X and XI present aerial concentrations of PCB congeners in Denver air. All PCB (peaks) listed are of the Group 1 type, except where noted. Levels of contaminants

chromatographing in the Aroclor 1242 region were quite high on filter blank A from October 1985 (Table VI and Figure 1) and most 1242-region congener concentrations are for the vapor phase only.

Also shown in Tables X and XI are concentrations of total PCB calculated as Aroclors using Method 1 and by summing the concentrations of the individual congeners found in the Aroclor 1242 or 1254 regions (Method 2). In the Aroclor 1242 region, total PCB concentrations obtained using the two methods agreed very well. A comparison of total PCB concentrations in the Aroclor 1254 region shows that concentrations obtained using Method 2 were consistently lower (76-88%) than those using Method 1. This difference occurred because there were a larger number of PCB peaks not identified by Capel et al. (e.g., P peaks in Figure 10) which contributed a substantial portion to the total 1254 concentration, since they are included in the Method 1 calculation. Capel et al. (71) observed that the percentage of total PCB using Method 2 ranged from 80-110% of those using Method 1 from more than 50 water, suspended solids, sediment and peat section samples. Our findings show that the Method 1 approach, which is routinely used for calculating levels of PCB in environmental samples, can provide good total PCB data for atmospheric samples.

Average January 1986 concentrations of total PCB in Denver (1.2 and 0.54 ng/m³ for Aroclor 1242 and 1254, respectively) were very similar to those determined in January 1980 (1.8 and 0.45 ng/m³) (19).



PAH in Denver Air

HPLC chromatograms of PAH on the filter, and PUF plugs from Denver sample D7 are shown in Figure 14, and chromatograms of filter blank C (January period) and a PAH standard are presented in Figure 15. No PAH were observed in the region of interest on any filter blank chromatograms. Plug 2 samples generally contained very little material due to minimal breakthrough of the 3-ring PAH from the first plug. Changes in retention times between sample injections were observed due to the poor reproducibility of the solvent programmer. However, overall chromatogram patterns were generally similar.

The D7 sample had the highest TSP concentration of any Denver sample, and because of suspected high PAH levels, selected peaks from the filter and plug 1 (Figure 14) were fractionated on the HPLC and qualitatively analyzed by GC-MS. Table XII shows PAH identified by GC-MS in fractionated peaks along with their base molecular ion. Identities of those compounds previously confirmed by GC-MS or fluorescence spectroscopy (14) to be major components in peaks eluting at nearly the same position in HPLC chromatograms of Columbia samples are denoted by an asterisk. Also listed are base ions of unknown components (with possible identities in brackets), which were found in the HPLC peaks by GC-MS but could not be positively identified without a standard.

HPLC peaks of D7 thought to be PH, B(k)F, B(ghi)P and coronene by pattern matching with previous Columbia filter

samples (14) were positively identified and appeared free of other coelutants. Peaks 4 and 5 were predominantly FLA and PY as previously assigned, but were also found to contain lesser amounts of components believed to be methyl phenanthrenes (MePH) or methyl anthracenes (MeAN). In the plug 1 extract, these methyl-substituted 3-ring PAH were also detected at higher levels in peaks identified as FLA and PY. Based on published fluorescence spectra of MePH (30), the methyl-substituted PAH probably contributed little to the total fluorescence of these peaks using our fluorimeter. Also FLA and PY were 70-90% recovered from SRM-1649 using the same fluorescence-HPLC procedure.

No anthracene was observed in the filter sample above the GC-MS detection limit. However, a compound having base m/e of 190 and suspected to be 4H-cyclopenta(def)-phenanthrene was found as the dominant component in the peak thought to be AN (peak 3) from previous work (14). The suspected 4H-cyclopenta(def)phenanthrene was also observed as the dominant component of peak 18 in plug 1, which contained only a trace amount of AN. In view of these findings, all HPLC peaks tentatively identified as AN in Denver samples may have, in fact, been dominated by the component with m/e of 190, and as a result no concentrations or partitioning ratios for AN are reported here.

Peak 11 contained INDENO, but also contained another component having a 276 base m/e, which comprised roughly 15% of peak 11 by GC-MS and an unknown amount by HPLC-fluorescence. Due to the unknown fluorescence

characteristics of the coeluting PAH, an approximate concentration of INDENO + Unknown is reported in Table XIII.

Of great concern was the inability to detect B(a)P in peak 8 by GC-MS. Pattern matching with Columbia air samples (14) suggested that peak 8 contained predominately B(a)P (base m/e = 252). This peak had been previously identified by GC-MS as B(a)P (or at least m/e = 252) in Columbia samples and confirmed using fluorescence spectroscopy (14). However, the D7 sample revealed only a very small amount of a component having base m/e of 242 (not 252) in peak 8. Amounts of B(k)F and B(ghi)P detected by GC-MS in peaks 7 and 10, were also very low, even though they were the only components present. This suggested that the isolation of PAH for GC-MS analysis from trapped LC bands may have not been complete. This was subsequently confirmed by recovery checks using a B(a)P standard fractionated on the HPLC and isolated from the mobile phase in an identical manner. A quantity of B(a)P easily measureable by HPLC-fluorescence was barely detectable by GC-MS. Based on the poor recovery of B(a)P from SRM-1649 (Table IV) and the lack of identification in D7 by GC-MS, B(a)P concentrations in Denver samples reported in Table XIII are tentatively considered lower limits.

As expected, concentrations of PAH in Denver air (Table XIII) were substantially higher on dirtier (high TSP) days. Wood smoke from domestic heating and petroleum sources were likely the major contributors to the atmospheric PAH burden during these cold weather sampling periods. Most

measurements of atmospheric PAH have been on airborne particles, with few measurements of individual PAH in the vapor phase (12-14,17,18). Average concentrations of individual PAH in Denver air were approximately equal to those in Columbia, SC (6) and Portland, OR (54) for some compounds, and up to three times higher for others, but were lower than levels reported for Tokyo (13). Countess et al. (20) reported an average B(a)P concentration in Denver air of 2.6 ng/m^3 for November-December 1978, which is about 50% higher than the 1.7 ng/m^3 average B(a)P concentration tentatively reported here. Greaves et al. (60) reported an average B(a)P concentration in Boulder air of 1.3 ng/m^3 for January 9, 10, and 12, 1985, which is comparable to the average concentration (2.5 ng/m^3) for January 6-10, 1986 reported here (Table XIV).

The one exception to the above findings was coronene, with an average concentration (6.1 ng/m^3) about 10 times higher than those found in Columbia or Portland, and more comparable to values reported by Grosjean (73), Gordon (74) and Gordon et al. (75) for Los Angeles. The high coronene levels are probably indicative of petroleum (vehicular) sources (43).

Table XIV compares average PAH concentrations in Boulder, CO reported by Greaves et al. (60), collected on January 9, 10, and 12, 1985 using low and high volume particle collectors, with average Denver concentrations for January 1986. Overall concentrations were comparable for heavy PAH, with the 5-ring compounds differing by no more

than a factor of three. However, concentrations of the 3-4 ring PAH were higher in 1986, especially PH which was higher by nearly a factor of 15. This large difference was due to our collection of 3-4 ring PAH in both the vapor and particle phases, whereas Greaves et al. used filter (particle) collection only.

Estimates of Vapor-Particle Partitioning in Denver Air

Separate analysis of organics on the PUF plugs and filters provided an opportunity to investigate the apparent vapor-particle partitioning for four classes of compounds: n-alkanes, organochlorine pesticides, PCB, and PAH.

Estimates of the apparent V/P partitioning can be obtained from the adsorbent-retained to filter-retained ratio (A/F). A/F ratios of individual compounds were related to the average sampling temperature (T, Kelvin) and the particle concentration (TSP, $\mu\text{g}/\text{m}^3$) using an expression derived by Yamasaki et al. (13):

$$\text{Log } A(\text{TSP})/F = m/T + b \quad (\text{Equation 2})$$

where m and b are constants of regression, and the A and F have units of ng/m^3 air. Bidleman and Foreman (16) have recently shown that this equation is essentially the same as the theoretical model of physical adsorption to aerosols presented by Junge (11, Appendix A):

$$\Phi = c\theta/(p^0 + c\theta) \quad (\text{Equation 3})$$

where $\Phi \{= 1/(1+X)\}$, where $X = A/F$ is the fraction of particle-bound SOC, p^0 is the solute saturation vapor

pressure, θ is the particle surface area in cm^2 per cm^3 of air available for adsorption, and c is a constant which depends on the heat of condensation and solute molecular weight. Equation 3 is applicable to systems where the partial pressure of the SOC is much smaller than its saturation vapor pressure, which is the case for the trace organic pollutants in this study.

Representative plots of Equation 2 for the four classes of compounds are shown in Figures 16-19. The n-alkanes from C-18 to C-23 were used. A/F of the higher molecular weight alkanes could not be determined, since these were rarely observed on PUF plugs under the cold sampling conditions in Denver. Only three PAH were considered, since identification of anthracene was uncertain and quantities of the 5-ring PAH on PUF were undetectable. Ten PCB congeners (or congener groups) chromatographing in the Aroclor 1254 region were selected, based on non-interference from other sample components, and their being detected reasonably well on both the filter and front plug. A/F of Aroclor 1254 calculated using Method 1 was also regressed versus $1/T$ for comparison with previous data. Inclusion of some congeners from the Aroclor 1242 region was desired, however low quantities on the filter coupled with the high amounts of contamination on filter blank A (October set) made this impossible.

A good deal of scatter was observed for a number of the compounds, as can be seen from the plots and the regression data (r^2 are listed in Table XV for those compounds not

Table XV, along with predicted A(TSP)/F at 5° and 20°. A(TSP)/F predicted at 5° have much tighter 95% confidence limits than those at 20°, since 20° was outside the data range (Figures 16-19). Predicted A(TSP)/F at both temperatures (Table XV) show an increasing vapor phase preference for compounds with higher vapor pressures (Table XVIII) as previously observed (6,8,49,53,54,55,59). A good example of this is shown by the PCB data in Table XV. Assuming a TSP concentration of 60 µg/m³, 2,5,3',4'-tetrachlorobiphenyl (IUPAC # 70) has a predicted A/F at 5°C of 6.6, giving $\Phi = 0.13$ (or 13% particle associated), whereas 2,3,4,5,2',4',5'-heptachlorobiphenyl (# 180) has an A/F at 5° of 0.14 resulting in $\Phi = 0.88$. The liquid phase vapor pressure (p_L^0) of 2,5,3',4'-tetrachlorobiphenyl at 5° is 3.8×10^{-6} , which is about a factor of 70 greater than the p_L^0 of the heptachlorobiphenyl (Table XVIII).

Table XVI presents a comparison of Equation 2 regression parameters and predicted A/F at 5° (TSP = 60 µg/m³) for five organochlorine SOC in this study with those reported by Bidleman et al. (15) for four cities (Columbia, Denver, Stockholm, Sweden, and New Bedford, MA). Upper and lower 95% confidence limits for the predicted values are also shown. Most of the samples collected by Bidleman et al. (15) were from Columbia and Stockholm, with only three samples collected in Denver in January 1980. Predicted A/F ratios at 5° from these two studies were different at the 95% confidence level for all the organochlorines except p,p'-DDT. In general, there was a greater percentage of

filter-retained SOC in Denver at a given TSP during the present investigation.

A similar comparison of Equation 2 regression parameters and predicted A/F ratios at 5° for several PAH is presented in Table XVII. Regression parameters reported by Keller and Bidleman (14), Yamasaki et al. (13), and Foreman and Bidleman (Chapter 1) were obtained using Equation 2. McVeety (17) did not measure TSP, and reported regression parameters for the equation:

$$\log A/F = m/T + b \quad (\text{Equation 4})$$

A TSP concentration of 60 $\mu\text{g}/\text{m}^3$ was selected for calculating the A/F ratios (not applicable for the data of McVeety). This TSP is lower than the average TSP observed during the present Denver study (84 $\mu\text{g}/\text{m}^3$) or by Yamasaki et al. (13) in Tokyo (127 $\mu\text{g}/\text{m}^3$), but it is higher than that observed in Columbia (42 $\mu\text{g}/\text{m}^3$) (14) or at the Savannah River Plant, SC (36 $\mu\text{g}/\text{m}^3$) (Chapter 1). Though not reported, TSP at Lake Siskiwit, on Isle Royale in northern Lake Superior (17), were probably even lower than those at SRP.

The comparisons drawn here are done so cautiously, since the limited data from Denver may be distorting the results. Predicted A/F at 5° in Denver and Tokyo were similar for all PAH, with somewhat lower A/F observed in Columbia. A/F at SRP was much lower than the other locations, but this may also be an artifact of the small data set from SRP (Chapter 1). Comparisons of A/F with the data of McVeety are difficult to assess, since TSP was not

measured at Lake Siskiwit (17).

Factors influencing differences in these A/F include those previously mentioned, especially temperature variability, unknown humidity effects, and difference in particle characteristics.

Site-to-site variability in the amount of non-exchangeable material on particles may also account for some of these differences. The non-exchangeable fraction is that portion of SOC strongly adsorbed to active sites on the particles or imbedded within the particle matrix, which is counted along with the exchangeable material adsorbed on or very near the particle surface (15,16,18). Non-exchangeable material would be unavailable for V/P exchange in the atmosphere, but would probably be included in the material extracted from the filter. This non-exchangeable SOC would result in an artificially lower A/F. Indications of non-exchangeable SOC on particles are provided by studies of PAH extraction from atmospheric particles (77-79) and fly ash (80), and adsorption studies of PAH to fly ash (81).

Previous field experiments (8,15,16) and a laboratory study (18) have shown that A/F partitioning is largely governed by the liquid-phase vapor pressures (p_L^O) of PAH and organochlorine pesticides and follows the empirical equation:

$$\log A(TSP)/F = m \log p_L^O + b \quad (\text{Equation 5})$$

Log A(TSP)/F for five PAH and seven organochlorines (six

pesticides and Aroclor 1254) correlated well with $\log p_L^0$ ($r^2 > 0.95$), but different lines were obtained from field results (16) and the laboratory studies (18)

Vapor pressures of the SOC are presented in Table XVIII. Except where noted, the PAH and pesticide vapor pressures are averages of those reported in the literature and summarized in an appendix to reference (82). Vapor pressures at 5° were estimated using vapor pressure versus $1/T$ correlations (Clapeyron equations if reported, or similar expressions derived from the GC method for determining vapor pressures (82)). Where required, solid- (p_S^0) and liquid-phase vapor pressures were interconverted using (83):

$$\ln p_L^0/p_S^0 = 6.8(T_m - T)/T \quad (\text{Equation 6})$$

where T_m is the melting point and T is the temperature of interest (both Kelvin) and 6.8 is a coefficient related to the entropy of fusion, as discussed in Chapter 1.

Vapor pressures of the PCB congeners and total PCB (Aroclor 1254) are those determined for the liquid phase by Foreman and Bidleman as described in (84, Chapter 2). These were extrapolated from 25° to 5° using vapor pressure-temperature relations obtained from the GC method (82).

p_L^0 for the n-alkanes are those reported by Duce and Gagosian (85). They calculated p_L^0 for C-18 to C-20 using appropriate constants found in Lange (86) for the Antoine equation. p_L^0 of higher molecular weight alkanes, were obtained by extrapolation of the C-1 to C-20 regression

line. p_L^O at the lower temperatures in this study were calculated using a factor of 1.8 decrease for every 5^O drop.

Figures 20-23 show plots of Equation 5 at 5^O C for n-alkanes, organochlorine pesticides, PAH, and PCB congeners, with regression parameters given in Table XIX. Predicted $A(TSP)/F$ at 5^O for individual compounds were obtained using the parameters from Equation 2 (Table XV). Upper and lower 95% confidence limits for the predicted $A(TSP)/F$ values obtained from the Equation 2 plots (Figures 16-19) are also shown in these plots. This temperature was selected because predicted $A(TSP)/F$ at 5^O are known with greater confidence than at 20^O , where previous correlations had been tested (15,16,18), since the latter temperature falls outside the data range.

Figure 24 is a replot of the PCB congener data of Figure 23 showing the 95% confidence bands of the mean predicted $A(TSP)/F$. Also shown in this figure is the predicted $A(TSP)/F$ for total PCB quantified as Aroclor 1254 using Method 1 (not included in the regression). The unusually large deviation of the total PCB from the line defined by the congeners was most surprising. Previous field studies had shown that Aroclor 1254 seemed to partition like the organochlorine pesticides (15, Chapter 3). However, this Aroclor 1254 point does not fall near the PCB, n-alkane, OC, or PAH lines (Figures 20-22) in this study or near the OC line from previous studies (15,18). The reason for this large deviation for total PCB is not completely understood. One possibility is that the overall

Aroclor 1254 vapor pressure is dominated by a few of the more volatile 1254-region congeners (84, Chapter 2), whereas the contribution of these lighter congeners to A/F partitioning of Aroclor 1254 in Denver appears to have been small.

Considering the amount of scatter in the Equation 2 plots from which the A(TSP)/F were obtained (probably the largest contributor to scatter in Figures 20-24) correlations between A(TSP)/F and p_L^O for the n-alkanes ($r^2 = 0.995$), PAH ($r^2 = 0.970$), pesticides ($r^2 = 0.948$), and PCB ($r^2 = 0.977$) were surprisingly good, although the data sets for PAH and pesticides were very small (Table XIX).

Figure 25 shows an Equation 5 plot combining all four classes of compounds, with regression parameters shown in Table XIX. The correlation for the combined data was also good ($r^2 = 0.958$), and statistical analysis of the Equation 5 plots (Figures 20-23 and Table XIX) revealed that the slopes for the four classes of compounds were not significantly different at the 95% confidence level. This finding suggests that A/F partitioning for the four classes of compounds in Denver at 5° could be adequately estimated using p_L^O of the SOC and the correlation in Figure 25.

Table XX presents a comparison of Equation 5 regression parameters at 20° observed in this investigation with those observed from field (15,16) and laboratory (18) studies. Both slopes and intercepts are lower here than observed in the previous studies for PAH and pesticides. However, 20° is outside the data range in this study, and predicted

$A(TSP)/F$ at 20° from which Equation 5 plots were derived are not known with a high degree of confidence.

CONCLUSIONS

This study has provided the first comprehensive measurement of a large number of individual PCB congeners in the atmosphere. In addition, it has also demonstrated that the widely used method of determining PCB concentrations by identification and quantification using a commercial PCB fluid standard (Method 1) can provide a very good estimate of the total PCB concentration in the air.

In general, concentrations of TSP, n-alkanes, organochlorine pesticides, PAH, and PCB were comparable to those observed in previous studies of Denver air and show that aerial concentrations of many of these contaminants are still reaching rather high levels during pollution events.

A/F ratios for n-alkanes, PAH, OC and PCB obtained during this study correlated reasonably well with the liquid phase vapor pressures of these compounds. Previous field and laboratory studies had suggested differences in partitioning between the PAH and organochlorines. However, due to the limited data set and scatter, this study was unable to confirm or deny these reported differences. The long times required for hi-vol sampling, and the attendant fluctuations in temperature, SOC concentrations, particle characteristics, etc., are considered primarily responsible for the large amount of scatter in the data. New low volume, short duration sampling methods for particles (60) and gases (12) should minimize many of the problems

associated with conventional hi-vol sampling. In addition, many of these new methods utilize thermal desorption techniques, which minimize sample handling and losses. Research using these new methods will be the next step in this investigator's exploration of the fundamental processes of vapor-particle partitioning.

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TABLE I

RECOVERIES OF n-ALKANES FROM SPIKED PUF.

n-alkane	Quantity μg	% Recovery ^a			
		Spike Sample No.			Mean \pm S.D.
		1	2	3	
12	10.25	57	49	55	53 \pm 4
14	9.48	58	50	55	54 \pm 4
16	1.91	66	60	66	64 \pm 3
18	6.39	80	78	76	78 \pm 2
20	7.38	104	107	106	106 \pm 2
22	6.39	108	111	113	111 \pm 2
24	7.71	102	104	109	105 \pm 4

^a Recoveries are averages of three injections quantified against the average of four standard injections.

TABLE II

RECOVERIES OF ORGANOCHLORINES FROM SPIKED PUF.

Compound	Quantity ng	% Recovery ^a			
		Spike Sample No.			Mean \pm S.D.
		1	2	3	
trans-chlordane	6.65	58	55	66	60 \pm 6
cis-chlordane	4.50	64	60	76	66 \pm 8
trans-nonachlor	5.45	71	66	73	70 \pm 4
p,p'-DDE	5.20	52	61	48	54 \pm 7
p,p'-DDT	12.0	98	102	96	99 \pm 3
Aroclor 1016	70.0	47	52	47	49 \pm 3
Aroclor 1254	59.5	63	69	62	65 \pm 4
toxaphene	372	87	88	73	83 \pm 8

^a Recoveries are averages of three injections quantified against the average of three or four (DDE, Aroclors 1016 and 1254) standard injections.

TABLE III

RECOVERIES OF PAH FROM SPIKED PUF.

Compound	Quantity μg	% Recovery ^a			
		Spike Sample No.			Mean \pm S.D.
		1	2	3	
PH	16.7	68	78	72	72 \pm 5
AN	0.506	69	75	72	72 \pm 3
FLA	4.14	77	86	83	82 \pm 5
PY	7.15	85	94	87	89 \pm 5
B(k)FLA	1.84	90	89	87	88 \pm 2
B(a)P	2.26	88	85	83	85 \pm 2
B(ghi)P	2.23	85	79	71	78 \pm 7
INDENO	2.44	83	77	73	78 \pm 5
COR	1.35	73	61	54	63 \pm 10

^a Recoveries are averages of two injections quantified against the average of three (PH, AN, FLA, PY) or two (other PAH) standard injections.



TABLE IV

RECOVERY OF PAH FROM URBAN DUST - SRM 1649.

	June 1986 Sample			Sept. 1984 SRM-1649 % Recovery ^e	
	1	2	3		
mg dust	199.68	194.08	207.14	(f)	
Compound	% Recovery ^a			Mean \pm S.D.	
				uncorrected	corrected ^b
FLA	74	86	83	81 \pm 6	99 \pm 9
PY	61	52	71	61 \pm 9	69 \pm 11
B(k)F	86	113	100	100 \pm 13	113 \pm 15
B(a)P	17	21	14	17 \pm 4	20 \pm 5
B(ghi)P + Di(ah)AN	73 ^c	82 ^c	76 ^c	77 \pm 5 ^c	98 \pm 10 ^d
INDENO	146	165	156	156 \pm 10	200 \pm 18

^a Recoveries are for single injections quantified against single injections of the standards.

^b Corrected for procedural loss (see TABLE III).

^c Benzo(ghi)perylene and dibenz(ah)anthracene coelute. Recoveries were calculated using the sum of these PAH in SRM-1649.

^d Corrected % recovery based on B(ghi)P spike recovery results (see TABLE III).

^e Recoveries for the Sept. 1984 analysis were for single injections quantified against three injections of the standard.

^f Sept. 1984 analysis of triplicate 150-200 mg dust samples.

TABLE V

DENVER SAMPLE COLLECTION DATA

Sample designation	Date	Temperature, °C			m ³ air	TSP μg/m ³
		max.	min.	avg.		
D1	7-8 Oct. 1985 ^a	23	2	12	892	48
D2	8-9 Oct. 1985 ^a	3	1	2	800	36
D3	9-10 Oct. 1985 ^a	12	2	5	915	88
D4	15-16 Oct. 1985 ^a	21	5	12	870	61
D5	6-7 Jan. 1986 ^b	3	0.7	2	520	27
D6	7 Jan. 1986 ^c	4	0.7	3	353	82
D7	7-8 Jan. 1986 ^b	1	-6	-4	554	157
D8	8-9 Jan. 1986 ^b	8	0.7	3	560	114
D9	9-10 Jan. 1986 ^b	6	1	3	554	143

^a Day-night sample.

^b Night only.

^c Daytime only

TABLE VI

COMPARISON OF CONTAMINANT QUANTITIES ON FILTER BLANKS (ng).^a

Sampling period	Oct. 1985		Jan. 1986			
Compound	Blank A		Blank B		Blank C	
octadecane	29	{4%}	<36 ^b		<33	
nonadecane	40	{3%}	<36		<33	
TEO ^c ≥C-19	2615	{0.3%}	1894	{0.2%}	733	{0.1%}
p,p'-DDE	0.06	{3%}	0.05	{1%}	0.04	{1%}
PCB ^d Congeners IUPAC No.						
7	2.7		1.2	{44%}	1.4	{51%}
46	3.9	{164%}	0.29	{21%}	0.21	{15%}
52	3.5	{130%}	0.28	{3%}	<0.59	
66	0.63	{24%}	0.24	{4%}	0.19	{3%}
110	0.61	{9%}	0.26	{2%}	0.28	{2%}
108,118,149	0.12	{2%}	0.13	{1%}	0.15	{1%}
146	0.07	{1%}	0.10	{1%}	0.08	{0.9%}
138,129	0.44	{3%}	0.11	{0.6%}	0.08	{0.4%}
Aroclor 1242 ^e	23	{88%}	8.6	{15%}	9.9	{17%}
Aroclor 1254 ^e	4.5	{4%}	1.7	{1%}	1.4	{1%}

^a Absolute amount on filter blank in ng. Values in brackets are the amount of material in filter blanks as a percentage of the average amount in sample set filters.

^b Less than values are limits of detection. Compound not observed.

^c Total extractable organics (nonpolar) ≥C-19 (see DISCUSSION section).

^d See Tables X and XI for PCB identifications.

^e Calculated using Method 1 (see DISCUSSION).

TABLE VII

CONCENTRATIONS OF n-ALKANES AND NONPOLAR TEO.

Compound	Sample								
	D1	D2	D3 ^b	D4	D5	D6	D7	D8	D9
n-alkanes (ng/m ³)									
18 ^a	26	34	66	38	31	51	49	42	71
19	17	18	33	24	16	28	24	22	36
20	12	12	19	18	9.8	18	17	16	25
21	15	7.4	9.2	15	6.5	13	14	10	17
22	9.8	4.1	3.2	12	2.9	1.3 ^b	8.7	6.0	8.9
23	5.9	3.2	0.8	6.6	2.1	4.5	7.6	6.0	8.6
24	2.8	1.9	--	4.8	1.3	5.0	6.2	2.2	4.3
25	2.9	1.5	--	3.3	1.7	NQ	9.9	4.6	6.7
26	3.0	2.4	--	2.6	0.7	4.0	7.8	1.7	11
27	6.5	2.2	--	3.7	0.9	3.0	12	3.7	6.0
28	2.7	0.5	--	0.8	0.2	3.6	6.5	4.3	7.2
29	19	2.7	--	7.6	0.8	5.2	12	4.6	12
30	3.0	1.3	--	4.3	1.7	NQ	9.4	3.9	12
31	7.2	2.5	--	4.5	1.2	6.2	4.1	7.6	10
32	1.4	0.9	--	1.1	0.2	3.7	4.4	NQ	2.6
nonpolar (fraction 1) TEO >C-19 (μg/m ³)	0.82	0.87	0.82 ^b	2.3	0.52	3.3	2.7	1.9	4.7
<u>Hydrocarbon preference index</u>									
A + F	1.7	1.2	--	1.2	1.2	--	1.1	--	1.0
Filter only	2.7	1.3	--	1.4	1.2	--	1.2	--	1.1

^a Corrected for procedural loss.^b Vapor phase (PUF) only.

NQ = not quantifiable.

TABLE VIII

COMPARISON OF AVERAGE n-ALKANE CONCENTRATIONS IN BOULDER, CO,
JANUARY 1985 AND DENVER, CO, JANUARY 1986.

	January 1986 ^a	January 1985 ^b
	Denver, CO	Boulder, CO
	(ng/m ³)	(ng/m ³)
$\Sigma C_{18}-C_{19}^c$	74	10
$\Sigma C_{20}-C_{21}$	29	16
$\Sigma C_{22}-C_{23}$	12	11
$\Sigma C_{24}-C_{32}$	46	28

^a Samples collected from January 6-10, 1986 (see Table V).

^b Samples collected on January 9, 10, and 12, 1985 by Greaves et al. (60), using one high and two low volume samplers on each date.

^c Sum of the average concentrations of C-18 and C-19, and similarly for the other groups.

TABLE IX
CONCENTRATIONS OF ORGANOCHLORINE PESTICIDES IN DENVER AIR (pg/m³). ^a

Compound	Sample								
	D1	D2	D3 ^b	D4	D5	D6	D7	D8	D9
t-CHLOR	20	14	38	57	16	21	44	19	47
c-CHLOR	19	12	30	47	17	24	39	17	39
t-NONA	12	5.9	16	27	10	15	21	10	27
p,p'-DDE	11	12	18	20	7.1	16	17	14	22
p,p'-DDT	12	7.6	7.0	23	4.4	14	19	30	24
toxaphene	≤45	≤50	≤60	≤131	≤20	≤77	≤146	≤107	≤169

^a Concentrations not corrected for procedural loss.

^b vapor phase only.

TABLE X

CONCENTRATIONS OF INDIVIDUAL PCB IN DENVER AIR - AROCLOR 1242 REGION (pg/m^3).^a

IUPAC No.	Cl(X) & H(O) substitution pattern	Sample								
		D1	D2	D3 ^b	D4	D5	D6	D7	D8	D9
7	XOXOO OOOOO	33	42	40	44	42	62	77	64	205
6	XOOOO OXOOO	33	51	77	74	38	76	92	92	102
8 ^c	XOOOO OOXOO	231	300	329	346	150	293	305	263	352
18	XOOXO XOOOO	213	197	195	439	99	198	375	268	435
16 [*] +32 ^d	XXOOO XOOOO XOOOX OOXOO	54	67	50	72	31	88	79	63	77
26	XOOXO OXOOO	24	19	30	35	17	NQ	NQ	NQ	NQ
25	XOXOO OXOOO	7.4	9.7	9.0	12	8.9	22	19	17	21
31 [*] +28 ^d	XOOXO OOXOO XOXOO OOXOO	85	95	88	129	63	121	90	89	115
33 ^c	OXXOO XOOOO	65	78	79	105	47	91	81	80	95
22	XXOOO OOXOO	21	20	21	31	13	22	22	21	26
52	XOOXO XOOXO	100	91	106	144	88	106	126	113	136
49	XOXOO XOOXO	79	70	81	99	54	69	85	75	109
47 [*] +48 ^d	XOXOO XOXOO XOXOO XOOOO	17	16	21	23	12	20	18	17	19
44	XXOOO XOOXO	41	34	40	65	36	53	50	43	62
37 [*] +42 ^e	OXXOO OOXOO XXOOO XOXOO	28	22	28	40	28	60	47	53	47
41 [*] +64 ^e	XXXOO XOOOO XXOOX OOXOO	34	32	38	46	32	48	46	37	58
40	XXOOO XXOOO	4.3	4.6	5.3	7.5	9.2	17	13	9.8	14
74	XOXXO OOXOO	14	14	17	21	11	20	24	20	24
Σ of congeners in Aroclor 1242 Method 2 (ng/m^3)		1.08	1.16	1.25 ^b	1.73	0.779	1.37	1.55	1.32	1.90
Aroclor 1242 ^f Method 1 (ng/m^3)		1.12	1.24	1.47 ^b	1.62	0.775	1.40	1.25	1.18	1.51

- a Not corrected for procedural loss.
- b Vapor phase only.
- c Group 2 - more than one congener in chromatographic peak, but the congener listed is dominant in Aroclor 1242.
- d Group 3 - two or more significant congeners in chromatographic peak, all listed. * denotes the major congener in Aroclor 1242.
- e Group 4 - more than one congener in chromatographic peak, but could not be further elucidated.
- f Concentrations obtained by summing areas of Aroclor 1242 region peaks in sample quantified versus an Aroclor 1242 standard (Method 1).

NQ = not quantifiable.

TABLE XI

CONCENTRATIONS OF INDIVIDUAL PCB IN DENVER AIR - AROCLOR 1254 REGION (pg/m³).^a

IUPAC No.	Cl(X) & H(O) substitution pattern	Sample								
		D1	D2	D3 ^b	D4	D5	D6	D7	D8	D9
70	XOXXO OXXOO	28	23	32	42	22	32	33	25	37
66	XOXOO OXXOO	47	35	53	36	37	50	51	44	60
60 [*] 56 ^c	XXXOO OOXOO XXOOO OXXOO	14	11	16	18	9.0	12	19	14	19
101	XOXXO XOOXO	73	55	74	122	62	70	83	70	102
83	XXOXO XXOOO	5.5	5.9	8.8	5.6	4.9	11	9.9	3.1	8.2
97	XOXXO XXOOO	12	10	20	19	13	15	19	11	18
110	XXOOX OXXOO	49	35	47	76	38	39	53	45	71
82	XXXOO XXOOO	11	8.8	13	14	8.1	8.6	12	8.3	15
118 [*] +108 +149 ^c	XOXXO OXXOO XXXOO OXOXO XXOOX XOXXO	33	24	28	53	25	28	42	31	55
146	XXOXO XOXXO	20	15	17	31	15	18	29	21	38
153	XOXXO XOXXO	8.4	7.2	7.7	14	6.9	9.2	14	11	17
141	XXXXO XOOXO	4.4	3.8	3.3	8.3	4.6	4.8	7.7	5.0	8.5
137	XXXXO XOXOO	0.8	1.2	1.6	1.8	0.8	1.4	2.5	0.9	2.5
138 [*] +129 ^c +unknown	XXXOO XOXXO XXXXO XXOOO	33	30	22	66	24	38	57	46	68
175	XXXOX XXOXO	20	18	11	35	11	22	32	25	40
187 [*] +159 ^c	XXOXX XOXXO XXXXO OXOXO	4.4	4.0	3.4	6.9	2.7	5.1	8.2	5.6	10
185	XXXXX XOOXO	4.2	3.4	2.2	6.1	2.6	4.5	6.6	5.3	9.7
180	XXXXO XOXXO	8.9	7.5	1.4	13	5.1	10	15	13	19
170	XXXXO XXXOO	6.3	4.1	0.9	7.4	3.2	5.4	8.0	8.1	13
Σ congeners in Aroclor 1254										
Method 2 (ng/m ³)		0.383	0.302	0.362 ^b	0.575	0.295	0.384	0.502	0.392	0.611
Aroclor 1254 ^d										
Method 1 (ng/m ³)		0.465	0.371	0.420 ^b	0.720	0.335	0.464	0.658	0.474	0.773

- a Not corrected for procedural loss.
- b Vapor phase only.
- c Group 3 - two or more significant congeners in chromatographic peak, all listed. * denotes the major congener in Aroclor 1254.
- d Concentrations obtained by summing areas of Aroclor 1254 region peaks in sample quantified versus an Aroclor 1254 standard (Method 1).

TABLE XII

GC-MS IDENTIFICATION OF PAH IN COLLECTED HPLC FRACTIONS
FROM DENVER SAMPLE D7.

LC band ^a	Component ^{b-d}	Base m/e	Relative ^e amount in HPLC band by GC-MS
<u>D7 Filter</u>			
1	[FL or phenalene] ^f	166	D
2	PH [*]	178	D
3	[4H-CYCLO]	190	D
	AN [*] not observed at LOD ^g		
4	FLA [*]	202	D
	[MePH or MeAN]	192	S
	[MePH or MeAN]	192	T
5	PY [*]	202	D
	[MePH or MeAN]	192	S
	unknown	202	T
6	[benzofluoranthene] ^h	252	D
	unknown	242	S
7	B(k)F [*]	252	D
8	[MeB(a)AN or MeCHRY]	242	D
	B(a)P [*] not observed at LOD		
9	unknown	276	D
10	B(ghi)P [*]	276	D
	Di(ah)AN not observed at LOD		
11	INDENO [*]	276	D
	unknown	276	S
12	not identified		
13	unknown	305	D

TABLE XII (continued)

GC-MS IDENTIFICATION OF PAH IN COLLECTED HPLC FRACTIONS
FROM DENVER SAMPLE D7.

LC band ^a	Component ^{b-d}	Base m/e	Relative ^e amount in HPLC band by GC-MS
<u>D7 Filter</u>			
14	unknown	300	D
	unknown	305	S
15	coronene [*]	300	D
<u>D7 Plug1</u>			
16	[FL or phenalene] ^f	166	D
17	PH [*]	178	D
	[MeFL or methyl phenalene]	180	T
	[MeFL or methyl phenalene]	180	T
18	AN [*]	178	T
	[4H-CYCLO]	190	D
	PH (carryover ?)	178	T
19	FLA [*]	202	S
	[MePH or MeAN]	192	S
	[dimethyl fluorene]	194	T
	unknown	204	T
20	unknown	198	S
	[MePH or MeAN]	192	S
	unknown	196	S
	unknown	196	S
	unknown	192	S

TABLE XII (continued)

GC-MS IDENTIFICATION OF PAH IN COLLECTED HPLC FRACTIONS
FROM DENVER SAMPLE D7.

LC band ^a	Component ^{b-d}	Base m/e	Relative ^e amount in HPLC band by GC-MS
<u>D7 plug 1</u>			
21	[MePH or MeAN]	192	D
	PY [*]	202	S
	[dimethyl fluorene]	194	T
22	unknown	184	S
	[DiMePH or DiMeAN]	206	S

^a See Figure 14.

^b Abbreviations are fluorene (FL), methyl fluorene (MeFL), phenanthrene (PH), anthracene (AN), methyl phenanthrene (MePH) or anthracene (MeAN), dimethyl phenanthrene (DiMePH) or anthracene (DiMeAN), 4H-cyclopenta(def)-phenanthrene (4H-CYCLO), fluoranthene (FLA), pyrene (PY), dimethyl benz(a)anthracene (DiMeB(a)AN), methyl chrysene (MeCHRY), benzo(k)fluoranthene (B(k)F), benzo(a)pyrene (B(a)P), benzo(ghi)perylene B(ghi)P, indeno(1,2,3-cd)pyrene (INDENO), and dibenz(ah)anthracene (Di(ah)AN).

^c Candidate PAH identities of unknown peaks in brackets.

^d * denotes major component identification normally attributed to the LC peak from previous studies by Keller and Bidleman (14).

^e D = Dominant component, S = component level substantial, T = present at trace level.

^f GC-MS retention time of filter peak 1 did not match the RT of the component identified in peak 16 of plug 1.

^g Compound not detected in band by GC-MS above the limit of detection.

^h The compound was not perylene or benzo(e)pyrene.

TABLE XIII

CONCENTRATIONS OF PAH IN DENVER AIR (ng/m³).^a

Compound	Sample									
	D1	D2	D3 ^b	D4	D5	D6	D7	D8	D9	
PH	14	21	45	39	24	35	56	43	72	
FLA	5.2	7.9	16	12	7.2	11	21	16	21	
PY	9.8	20	42	28	17	14	32	21	28	
B(k)F	0.23	0.24	--	0.39	0.19	0.48	2.3	1.1	1.7	
B(a)P ^c	≥0.26	≥0.20	--	≥0.71	≥0.23	≥0.68	≥4.6	≥2.9	≥3.9	
B(ghi)P + D(ah)AN	1.1	1.4	--	2.3	1.6	3.0	9.4	6.2	8.6	
INDENO + unknown	0.95	0.97	--	1.6	1.1	2.5	10	4.9	6.8	
COR	1.4	1.4	--	2.8	1.2	2.5	9.4	14	16	

^a Concentrations not corrected for procedural losses.^b vapor phase (PUF) only.^c Lower limit, see DISCUSSION section.

TABLE XIV

COMPARISON OF AVERAGE PAH CONCENTRATIONS IN BOULDER, CO,
JANUARY 1985 AND DENVER, CO, JANUARY 1986.

	January 1986 ^a Denver, CO (ng/m ³)	January 1985 ^b Boulder, CO (ng/m ³)
PH	46 ± 19	3.1
FLA	15 ± 6	5.3
PY	22 ± 8	5.0
B(k)F	1.2 ± 0.9	2.4 ^c
B(a)P	≥2.5 ± 1.9	1.3
B(ghi)P	5.8 ± 3.4 ^d	1.8
IDENO	5.1 ± 2.8 ^e	2.8
COR	8.6 ± 6.4	NR

^a Samples collected from January 6-10, 1986 (see Table V).

^b Samples collected on January 9, 10, and 12, 1985 by Greaves et al. (60), using one high volume and two low volume samplers on each date.

^c Also includes B(b)F.

^d May also include some Di(ah)AN (see DISCUSSION section).

^e Also contains an unknown PAH (see DISCUSSION section).

TABLE XV

REGRESSION PARAMETERS FOR PLOTS OF $\log A(TSP)/F$ VERSUS $1/T$.^a

Compound	m	b	r ²	n	Predicted log A(TSP)/F ^b	
					5°C	20°C
<u>n-alkanes</u>						
C-18	-1637	9.026	0.325	8	3.142	3.443
C-19	-1431	7.864	0.278	8	2.721	2.984
C-20	-1279	6.869	0.197	8	2.270	2.506
C-21	-3836	15.673	0.851	8	1.884	2.590
C-22	-6563	25.083	0.940	7	1.489	2.697
C-23	-6010	22.678	0.928	4	1.072	2.178
<u>pesticides</u>						
<u>trans</u> -chlordane	-1996	9.714	0.234	8	2.655	3.017
<u>cis</u> -chlordane	-2002	9.764	0.360	8	2.565	2.934
<u>trans</u> -nonachlor	-1886	9.158	0.200	8	2.377	2.724
p,p'-DDE	-2905	12.706	0.713	8	2.263	2.797
p,p'-DDT	-3456	13.973	0.461	8	1.548	2.184
<u>PAH</u>						
phenanthrene	-2033	10.989	0.391	5	3.681	4.055
fluoranthene	-2581	12.064	0.709	7	2.784	3.259
pyrene	-3722	16.190	0.618	7	2.808	3.493

TABLE XV (continued)

REGRESSION PARAMETERS FOR PLOTS OF $\log A(TSP)/F$ VERSUS $1/T$.^a

Compound	m	b	r^2	n	Predicted $\log A(TSP)/F^b$	
					5°C	20°C
PCB ^c						
70	-2598	13.232	0.597	8	2.597	3.142
66	-2743	12.529	0.616	8	2.669	3.174
101	-3167	13.889	0.721	8	2.503	3.085
110	-3296	14.132	0.765	8	2.828	2.889
82	-2362	10.815	0.491	8	2.325	2.759
108,118,149	-2751	11.883	0.685	8	1.994	2.500
146	-3215	13.360	0.738	8	1.802	2.393
153	-2644	11.271	0.570	8	1.765	2.251
175	-3065	12.660	0.535	8	1.641	2.205
180	-4765	18.052	0.737	8	0.9216	1.798
Aroclor 1254 ^d	-2312	10.322	0.598	8	2.010	2.435

^a Parameters for Equation 2.^b Units of $A(TSP)/F$ are $\text{ng Z/m}^3 \text{ air} \div \text{ng Z}/\mu\text{g particles}$, where Z represents an individual pollutant.^c PCB identifications given in TABLES X and XI.^d A/F ratios determined from concentrations of Aroclor 1254 using Method 1 (see DISCUSSION).

TABLE XVI

COMPARISON OF EQUATION 2 REGRESSION PARAMETERS AND PREDICTED A/F FOR SEVERAL PESTICIDES AND PCB WITH LITERATURE VALUES.

					Predicted A/F at 5 ⁰ (TSP = 60 μg/m ³)		
					95% confidence limits		
	<u>m</u>	<u>b</u>	<u>r²</u>	<u>n</u>	<u>A/F</u>	<u>Lower</u>	<u>Upper</u>
<u>t-CHLOR</u>							
this work	-1996	9.714	0.234	8	7.5	4.4	13
Bidleman ^{a,b} <u>et al.</u> (15)	-4995	21.010	0.881	15	18	12	24
<u>c-CHLOR</u>							
this work	-2002	9.764	0.360	8	6.1	4.1	9.2
Bidleman ^{a,b} <u>et al.</u> (15)	-4995	21.010	0.881	15	18	12	24
<u>p,p'-DDE</u>							
this work	-2905	12.706	0.713	8	3.1	2.3	4.0
Bidleman ^a <u>et al.</u> (15)	-5114	21.048	0.881	15	7.5	4.9	11
<u>p,p'-DDT</u>							
this work	-3456	13.973	0.461	8	0.59	0.33	1.0
Bidleman ^a <u>et al.</u> (15)	-5870	22.824	0.885	18	0.85	0.58	1.1
<u>Aroclor 1254^c</u>							
this work	-2312	10.322	0.598	8	1.7	1.3	2.3
Bidleman ^a <u>et al.</u> (15)	-4686	19.428	0.885	34	6.2	5.2	7.8

- ^a Data of Bidleman et al. (15) include samples collected from the following cities: Columbia, SC (1977-82); Denver, CO (January 1980); Stockholm, Sweden (1983-85), and New Bedford, MA (June 1980 - Aroclor 1254 only).
- ^b The Equation 2 parameters chlordanes reported by Bidleman et al. include cis- + trans-chlordane + trans-nonachlor.
- ^c Calculated using Method 1 (see DISCUSSION).

TABLE XVII

COMPARISON OF EQUATION 2 REGRESSION PARAMETERS AND PREDICTED A/F RATIOS FOR SEVERAL PAH WITH LITERATURE VALUES.

					Predicted A/F at 5° (TSP = 60 μg/m³)	
	m	b	r²	n	A/F	95% confidence limits lower-upper
<u>phenanthrene</u>						
this work	-2.03E+3	10.99	0.391	5	80	(37-172)
Yamasaki ^a <u>et al.</u> : (13)	-4.12E+3	18.45 ^b	0.776	22	73	
McVeety (17) ^d	-3.50E+3	14.3	0.92	21	51 ^d	
<u>fluoranthene</u>						
this work	-2.58E+3	12.06	0.709	7	10	(7.7-13)
SRP (Chapter 1)	-7.29E+3	27.91	0.933	8	0.81	
Keller ^c <u>et al.</u> : (14)	-5.18E+3	20.80	0.682	13	2.4	
Yamasaki <u>et al.</u> : (13)	-4.42E+3	18.52 ^b	0.805	27	7.0	
McVeety (17) ^d	-3.67E+3	14.1	0.90	21	7.9 ^d	
<u>pyrene</u>						
this work	-3.72E+3	16.19	0.618	7	11	(6.6-17)
SRP (Chapter 1)	-7.32E+3	27.64	0.704	8	0.34	
Keller <u>et al.</u> : (14)	-4.51E+3	18.48	0.695	11	3.0	
Yamasaki <u>et al.</u> : (13)	-4.18E+3	17.55 ^b	0.796	27	5.4	
McVeety (17) ^d	-3.82E+3	14.5	0.90	21	5.7 ^d	

- a Yamasaki et al. (13) collected samples in Tokyo, Japan. They were unable to distinguish between phenanthrene and anthracene using GC, and Equation 2 parameters were calculated using the combined concentrations of these two PAH on the PUF plugs and filter.
- b Yamasaki et al. reported b values 1000 times greater, with TSP expressed in ng/m^3 . These b values were recalculated with TSP in $\mu\text{g}/\text{m}^3$.
- c Keller et al. (14) collected data in Columbia, SC.
- d McVeety et al. (17) collected data in Lake Siskiwit, on Isle Royale in northern Lake Superior. McVeety did not measure TSP, and therefore the regression parameters and predicted A/F were obtained using the model:
 $\log A/F = m/T + b$.

- ^a Unless otherwise noted, solid phase vapor pressures are averages of those reported in the literature and summarized in (82). Extrapolations to lower temperature were made using Clapeyron equations reported in the literature for these SOC.
- ^b p_L^O for the chlordanes were determined using a GC method (82,87). p_S^O were estimated from p_L^O using Equation 6.
- ^c PCB congener identifications given in Tables X and XI.
- ^d p_L^O for PCB are taken from (84), extrapolated to lower temperatures using temperature- p_L^O relations derived using the GC method for determining vapor pressures (82). p_S^O were estimated from p_L^O using Equation 6.
- ^e All PCB boiling point data were calculated by Shiu and Mackay (88).
- ^f p_L^O for n-alkanes taken from Duce and Gagosian (85), with values at lower temperatures estimated using a factor of 1.8 decrease for every 5° temperature drop.

TABLE XIX

REGRESSION PARAMETERS FOR PLOTS OF $\log A(TSP)/F$ VERSUS $\log p_L^o$ AT 5°C .^a

Compound class	<u>m</u>	<u>b</u>	<u>r²</u>	<u>n</u>
n-alkanes	0.8616	7.286	0.995	6
PAH	0.8374	6.873	0.970	3
Organochlorine pesticides	0.7482	6.709	0.948	4
PCB ^b	0.9527	7.881	0.977	10
Combined ^c n-alkanes + PAH + PCB + pesticides	0.7787	6.796	0.958	23

^a Regression parameters for Equation 5.

^b PCB include those congeners listed in Table XV.

^c Plot constructed using data for the four classes of compounds.

TABLE XX

COMPARISON OF REGRESSION PARAMETERS FOR PLOTS OF $\log A(TSP)/F$ VERSUS $\log p_L^O$ AT 20°C WITH LITERATURE VALUES.^a

	<u>m</u>	<u>b</u>	<u>r²</u>	<u>n</u>
<u>PAH</u>				
this study	0.667	6.207	0.993	3
Bidleman et al. (15) field study	0.897	7.090	0.961	7
Foreman et al. (18) laboratory study	1.299	9.140	0.904	4
<u>Organochlorine pesticides</u>				
this study	0.600	5.738	0.999	4
Bidleman et al. (15) field study	0.769	7.311	0.956	6
Foreman et al. (18) laboratory study	0.983	8.531	0.998	7
<u>PCB^b</u>				
this study	0.883	7.259	0.961	10

^a Regression parameters for Equation 5.

^b PCB include those congeners listed in Table XV.

Figure 1. GC-ECD chromatograms of the non-polar fraction
for Filter Blanks C (January period) and A
(October period).

1 = HCB, 2 = heptachlor, 3 = p,p'-DDE

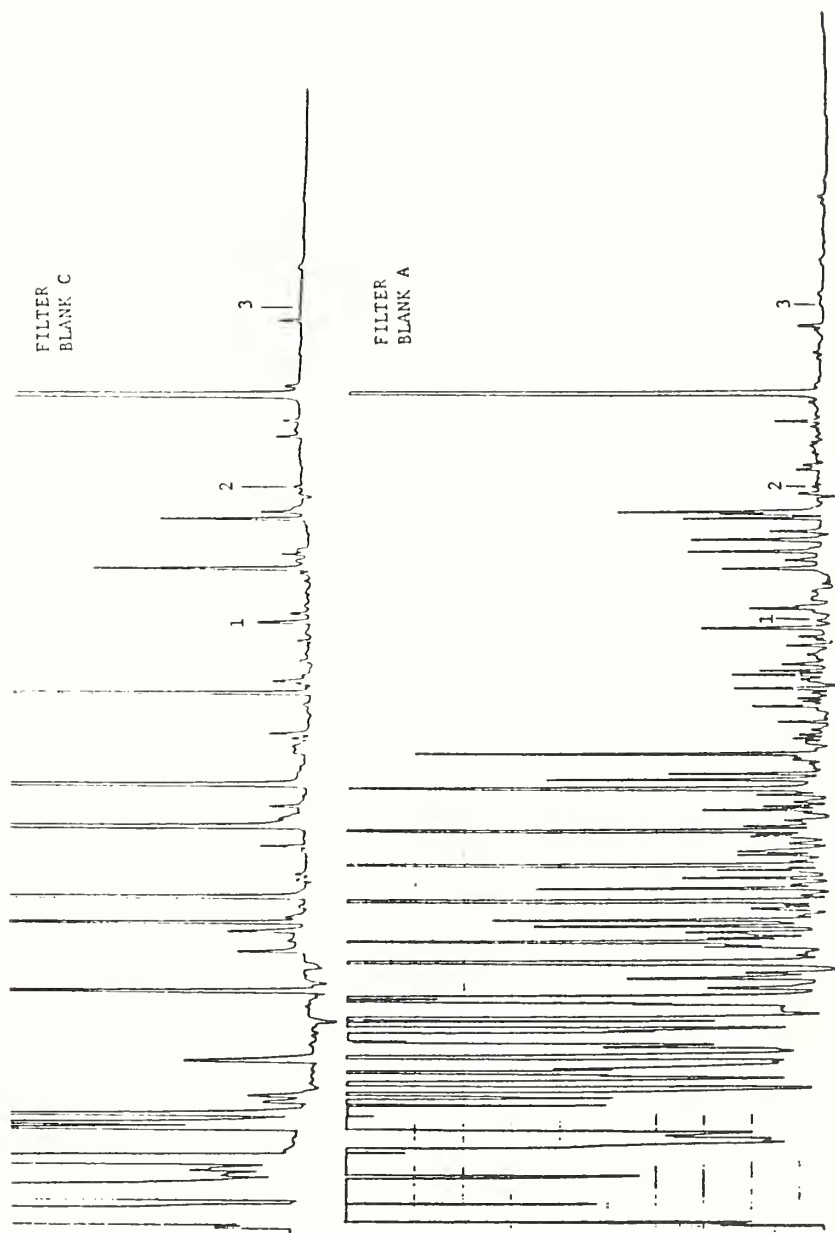


Figure 2. GC-FID chromatograms of the non-polar fraction for Denver sample D1. Carbon numbers for some n-alkanes are shown. Pr = pristane, Ph = phytane, IS = internal standard.

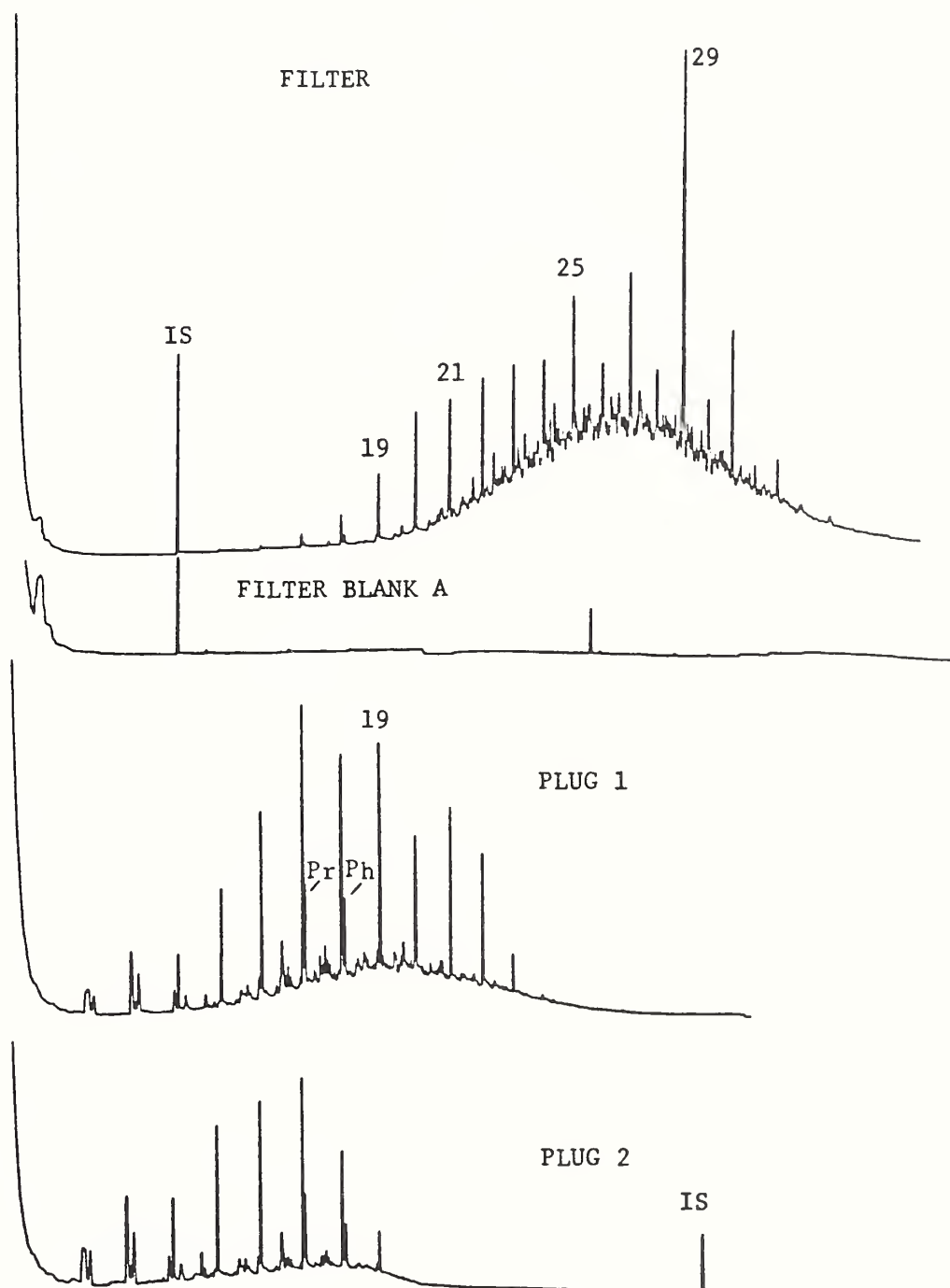


Figure 3. GC-FID chromatograms of the non-polar fraction for Denver sample D4. Carbon numbers for some n-alkanes are shown. Pr = pristane, Ph = phytane, IS = internal standard.

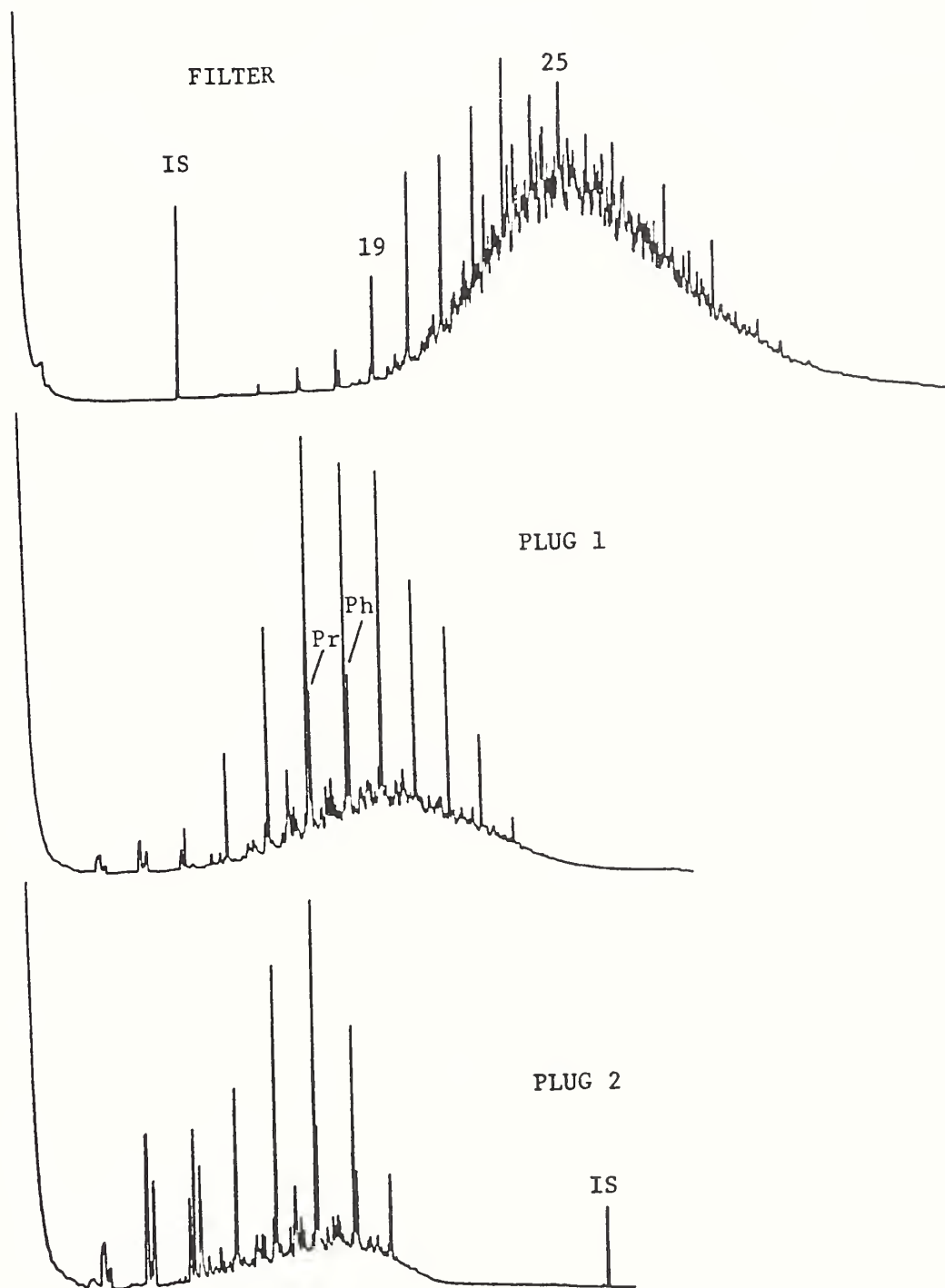


Figure 4. GC-FID chromatograms of the non-polar fraction for Denver sample D7. Carbon numbers for some n-alkanes are shown. Pr = pristane, Ph = phytane, IS = internal standard.

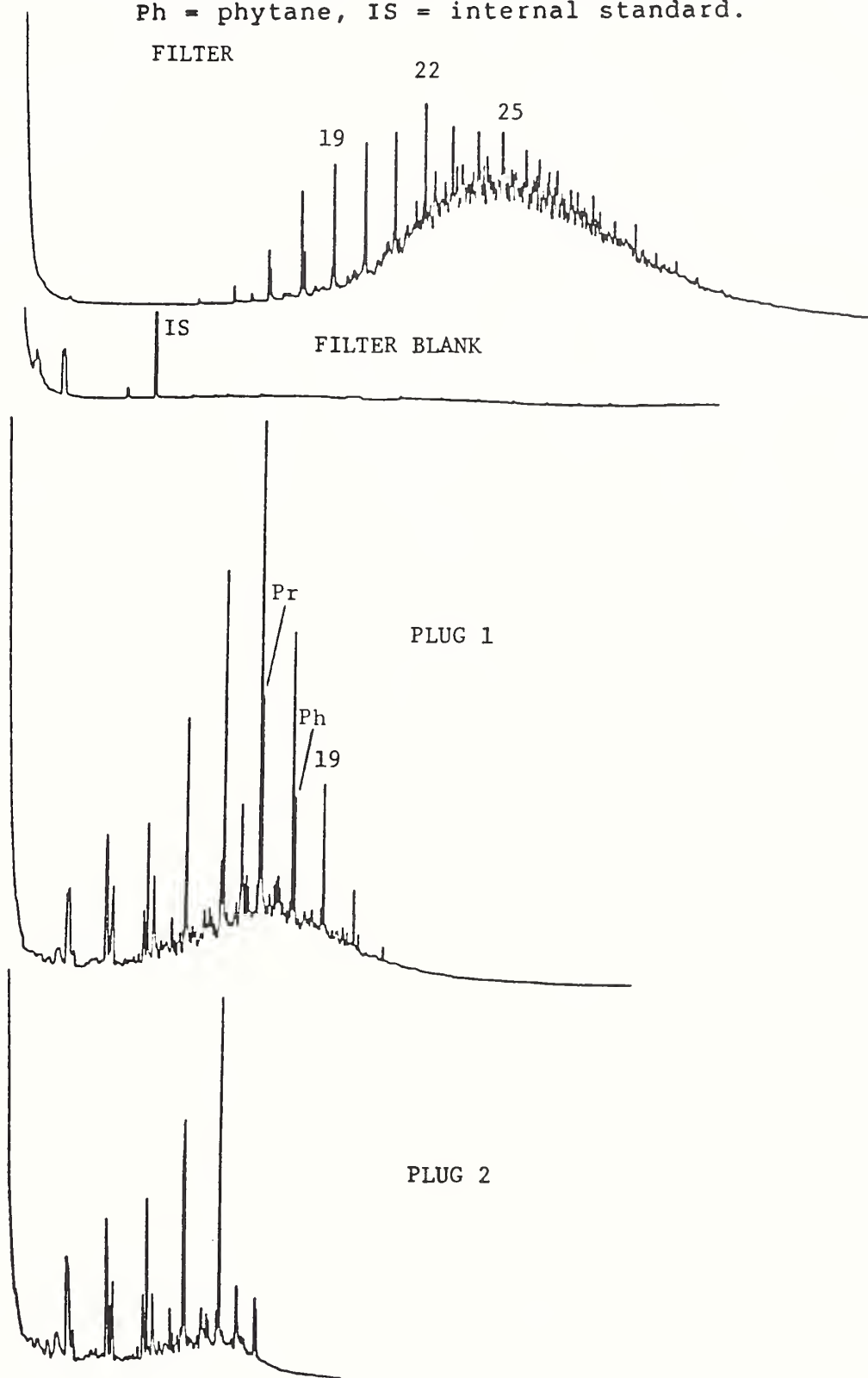


Figure 5. GC-ECD chromatograms of the polar fraction
for Denver sample D7, and a toxaphene standard.
1 = trans-chlordane, 2 = cis-chlordane
3 = trans-nonachlor, 4 = p,p'-DDT

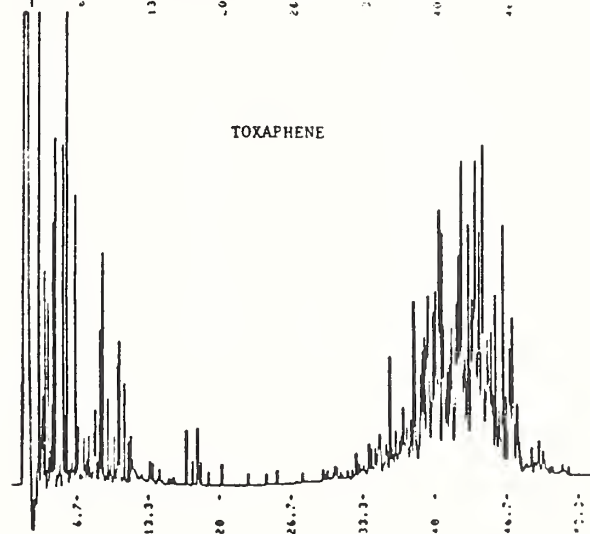
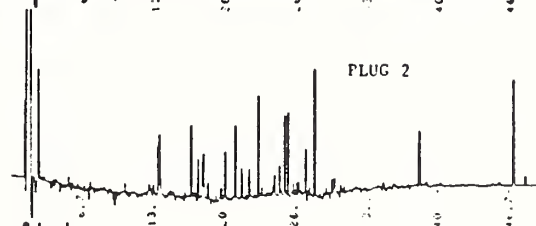
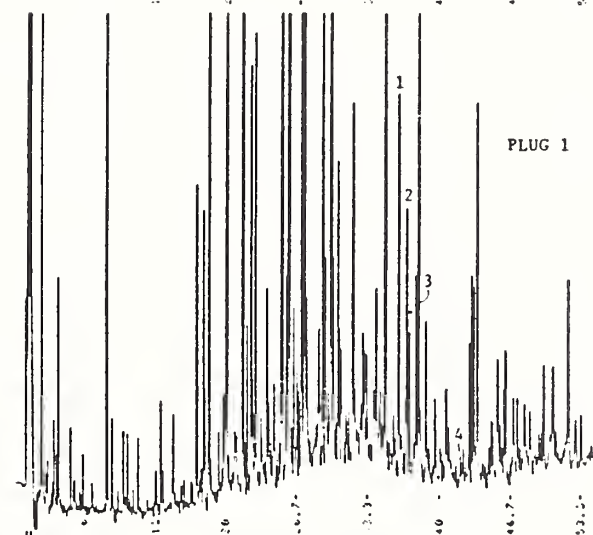
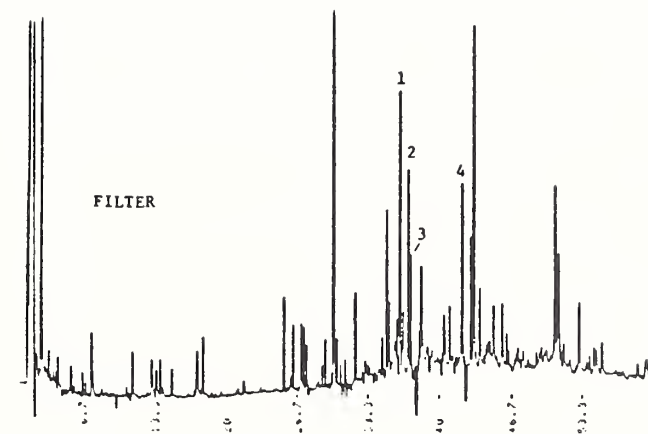


Figure 6. GC-ECD chromatograms of the polar fraction for Filter Blank C (January period) and a mixed pesticide standard.

1 = trans-chlordane, 2 = cis-chlordane
3 = trans-nonachlor, 4 = p,p'-DDT

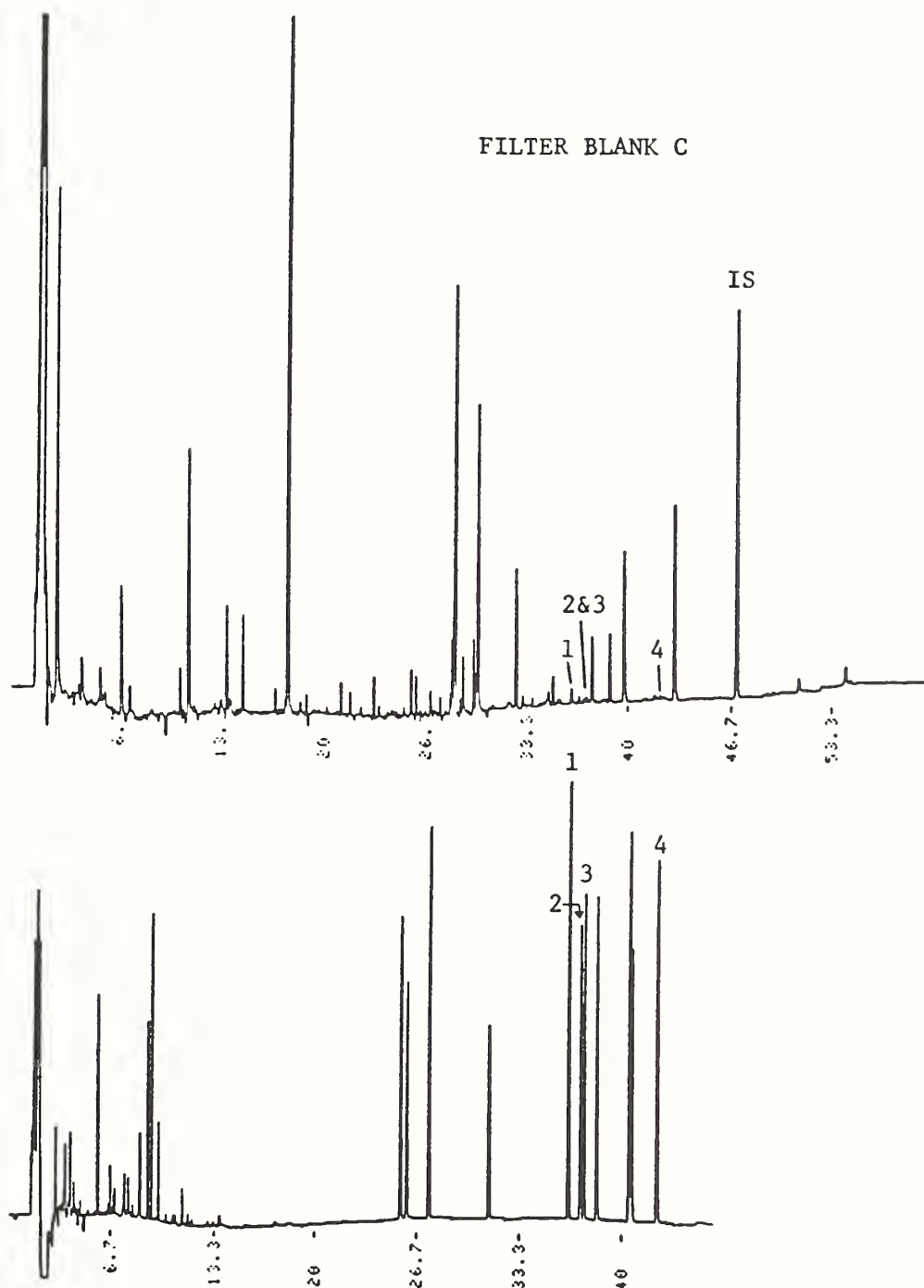


Figure 7a. Hexachloro- through nonachloro-toxaphene components in Denver sample D4 filter plus front plug by GC-NCIMS.

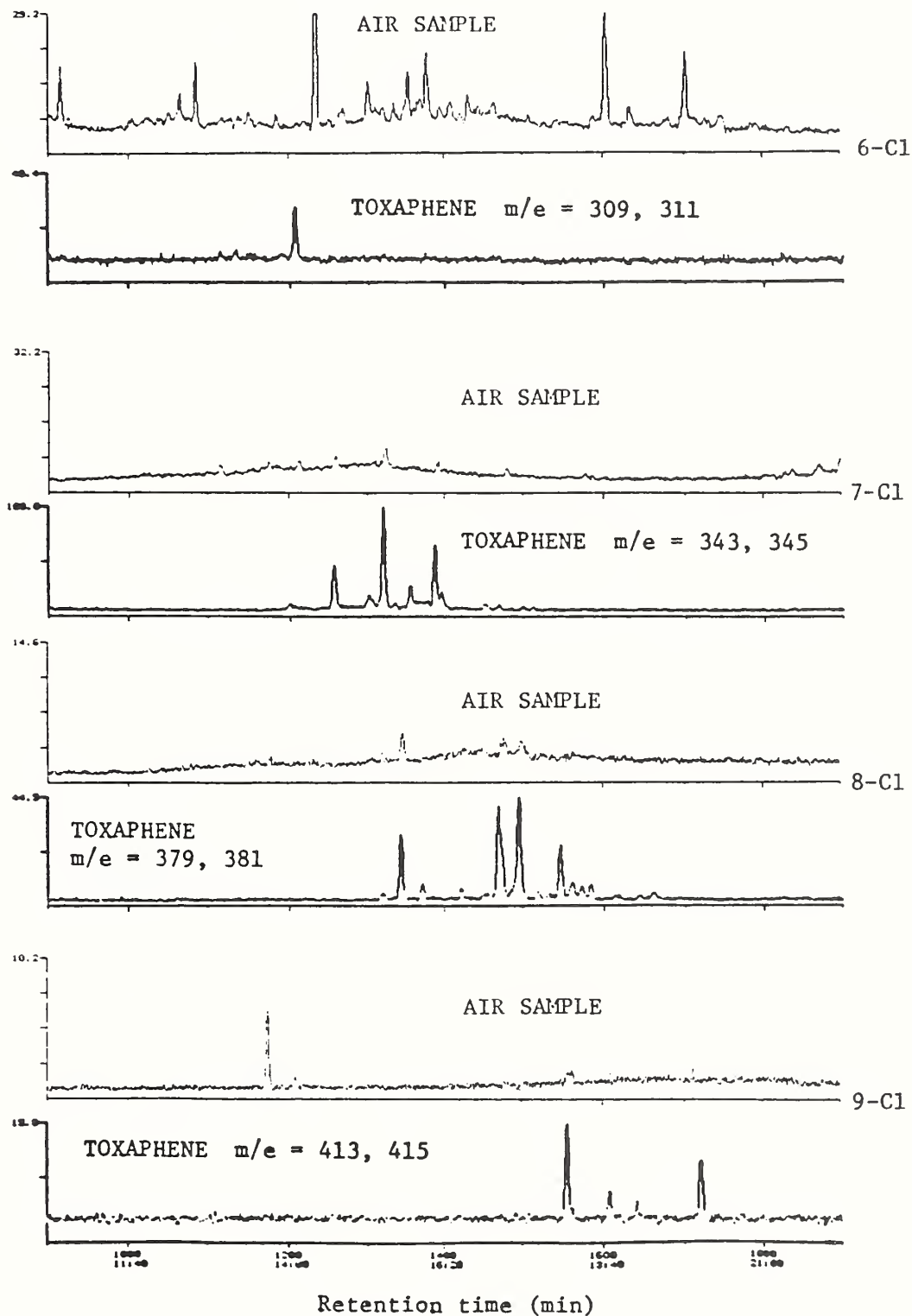


Figure 7b. Hexachloro- through nonachloro-toxaphene components in Denver sample D9 filter plus front plug by GC-NCIMS.

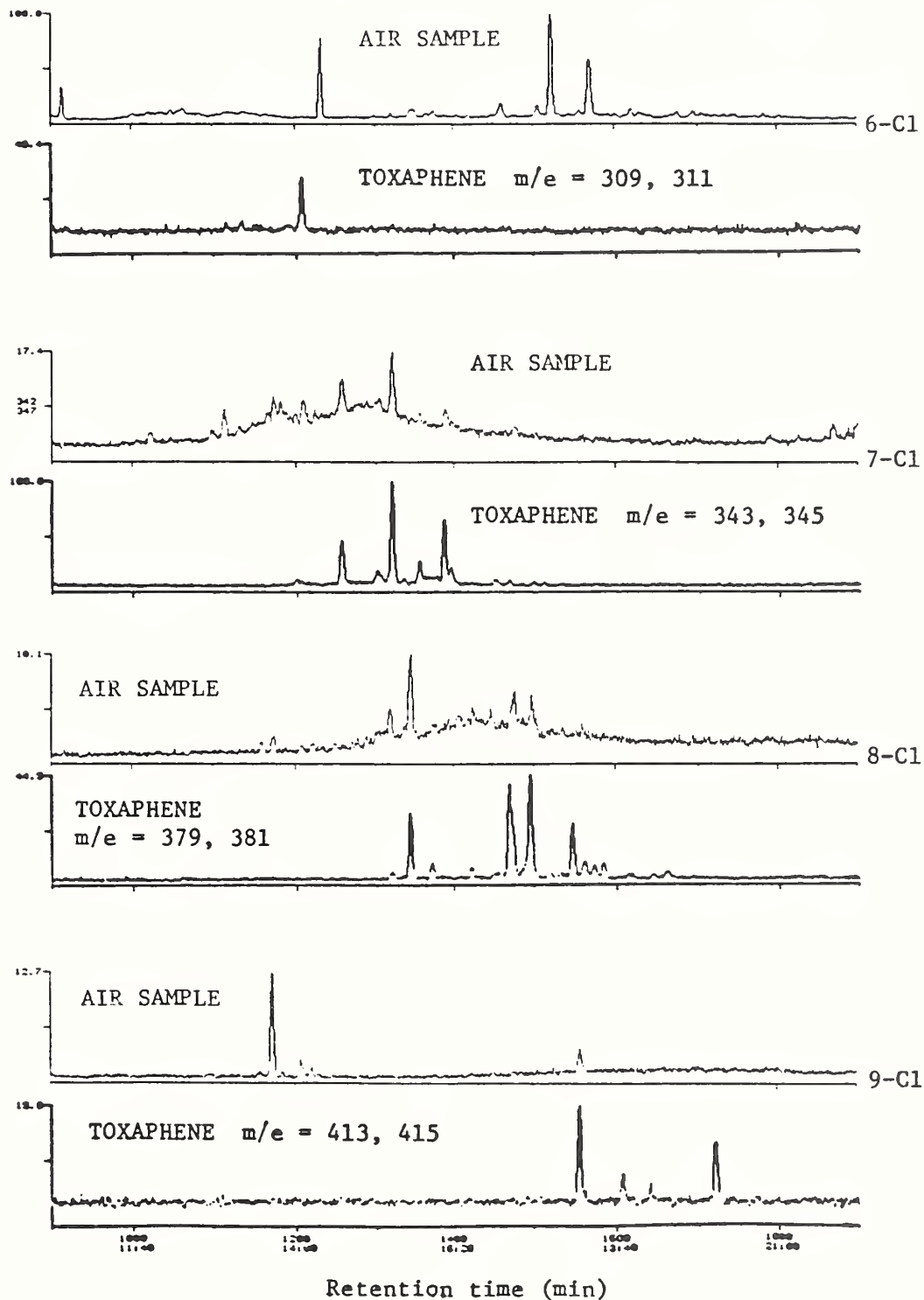


Figure 7c. Hexachloro- through nonachloro-toxaphene components in Denver sample D9 back-up plug plus filter blank C by GC-NCIMS.

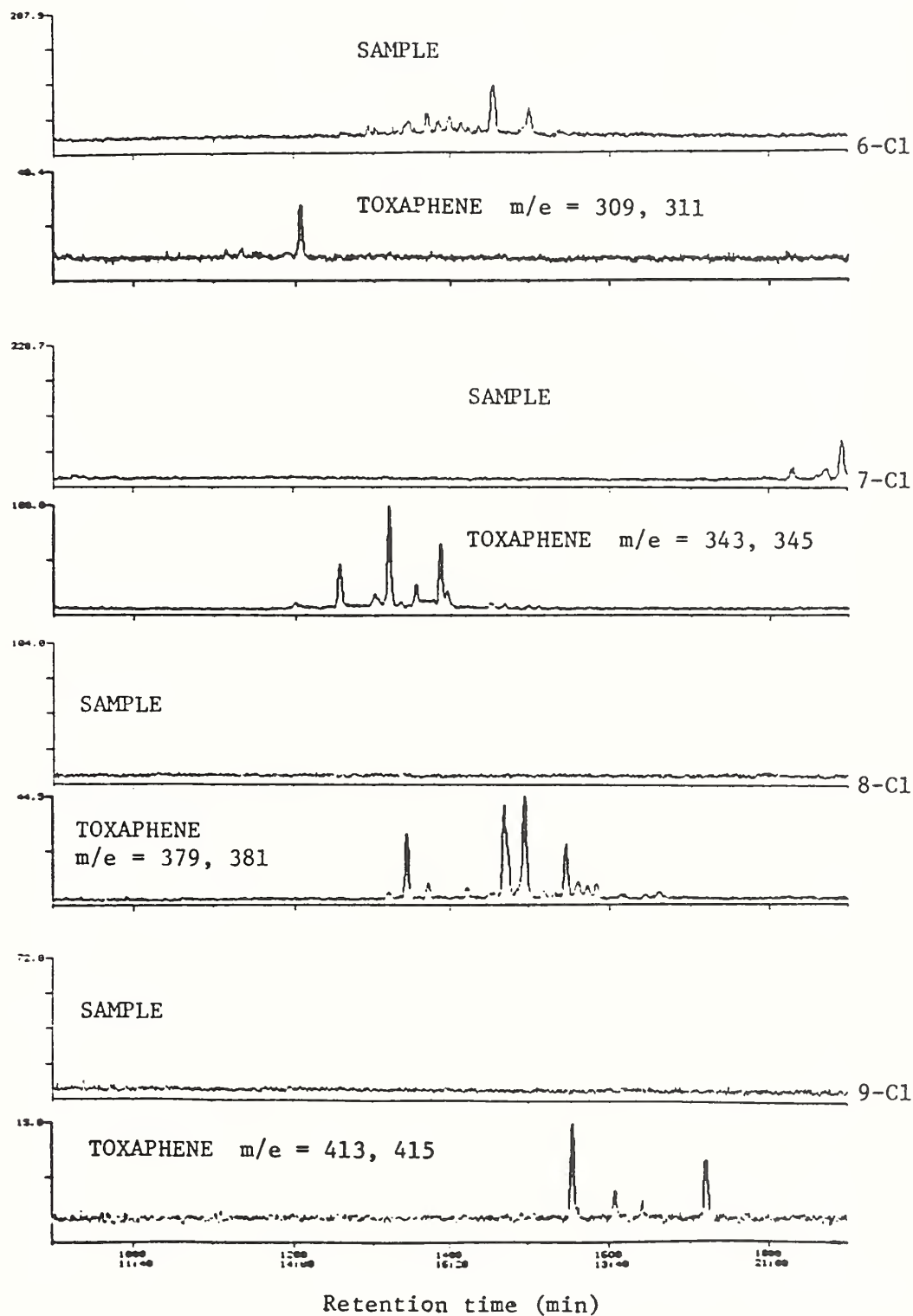


Figure 8. GC-ECD chromatogram of Aroclor 1242 standard. Peak identifications given in Table X.

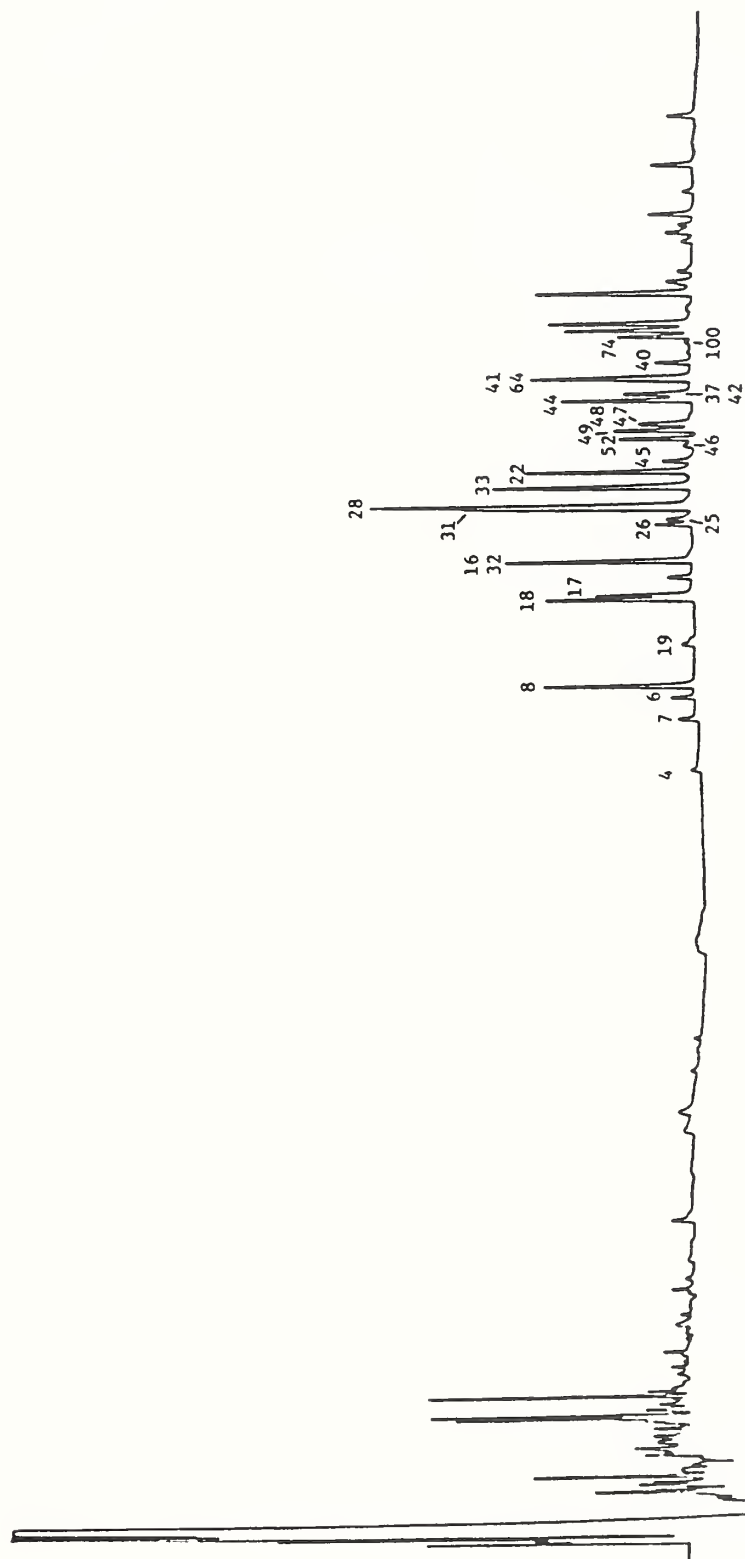


Figure 9. GC-ECD chromatogram of an Aroclor 1242 and 1254 mixed standard. Aroclor 1254 peak identifications given in Table XI.

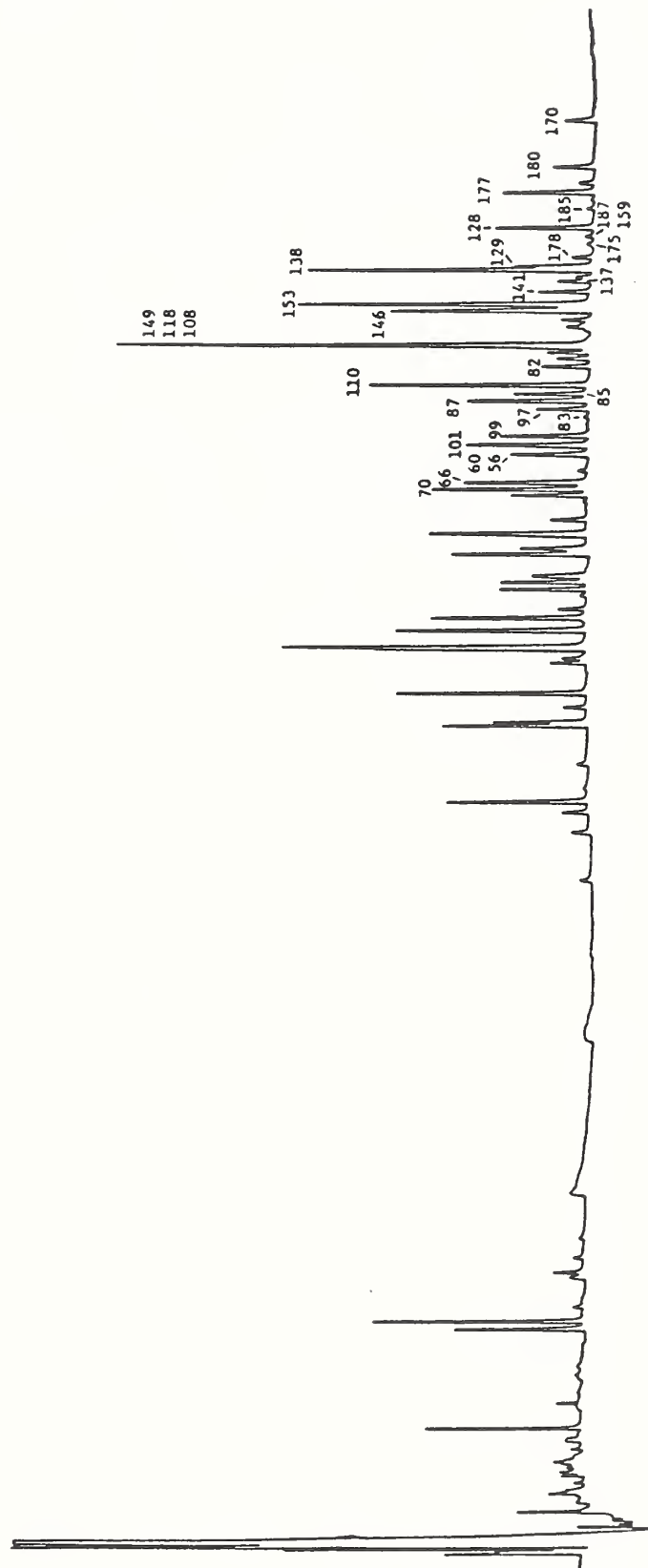


Figure 10. GC-ECD chromatograms of the non-polar (PCB) fraction for the filter and front plug from Denver sample D8. Peak identifications given in Tables X and XI.

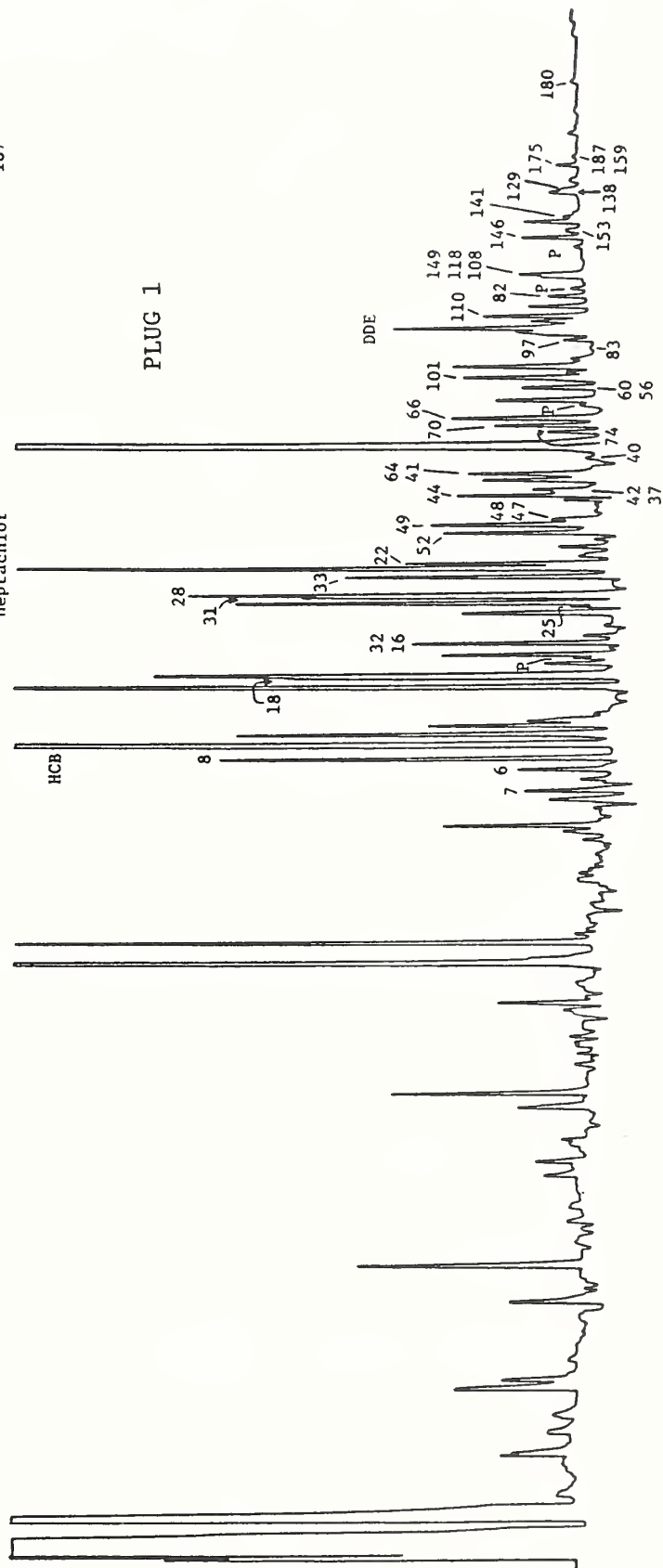
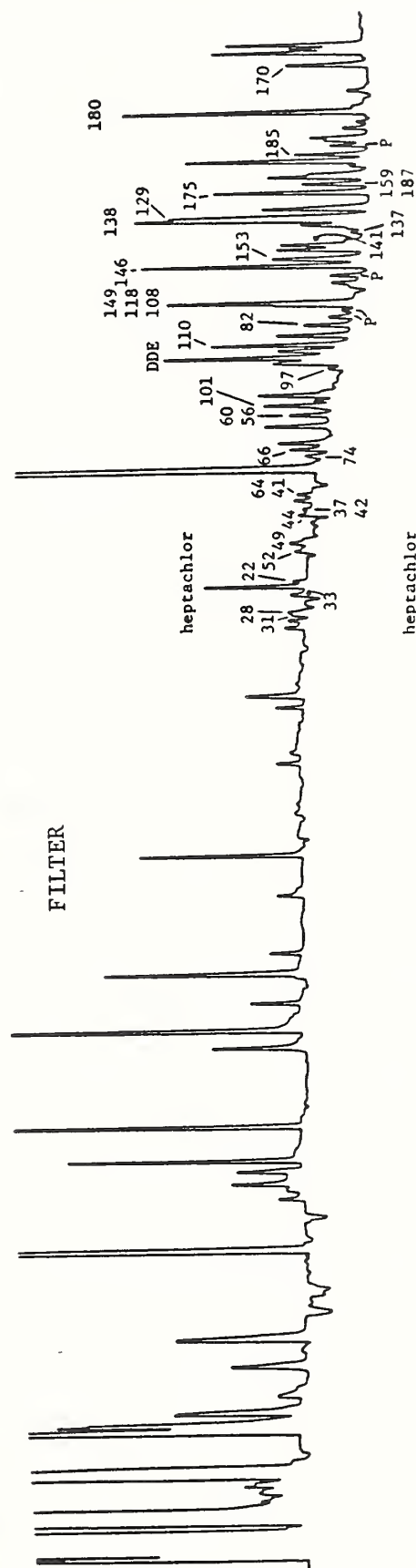


Figure 11. GC-ECD chromatograms of the non-polar (PCB) fraction for Filter Blank C and the back-up plug from Denver sample D8.

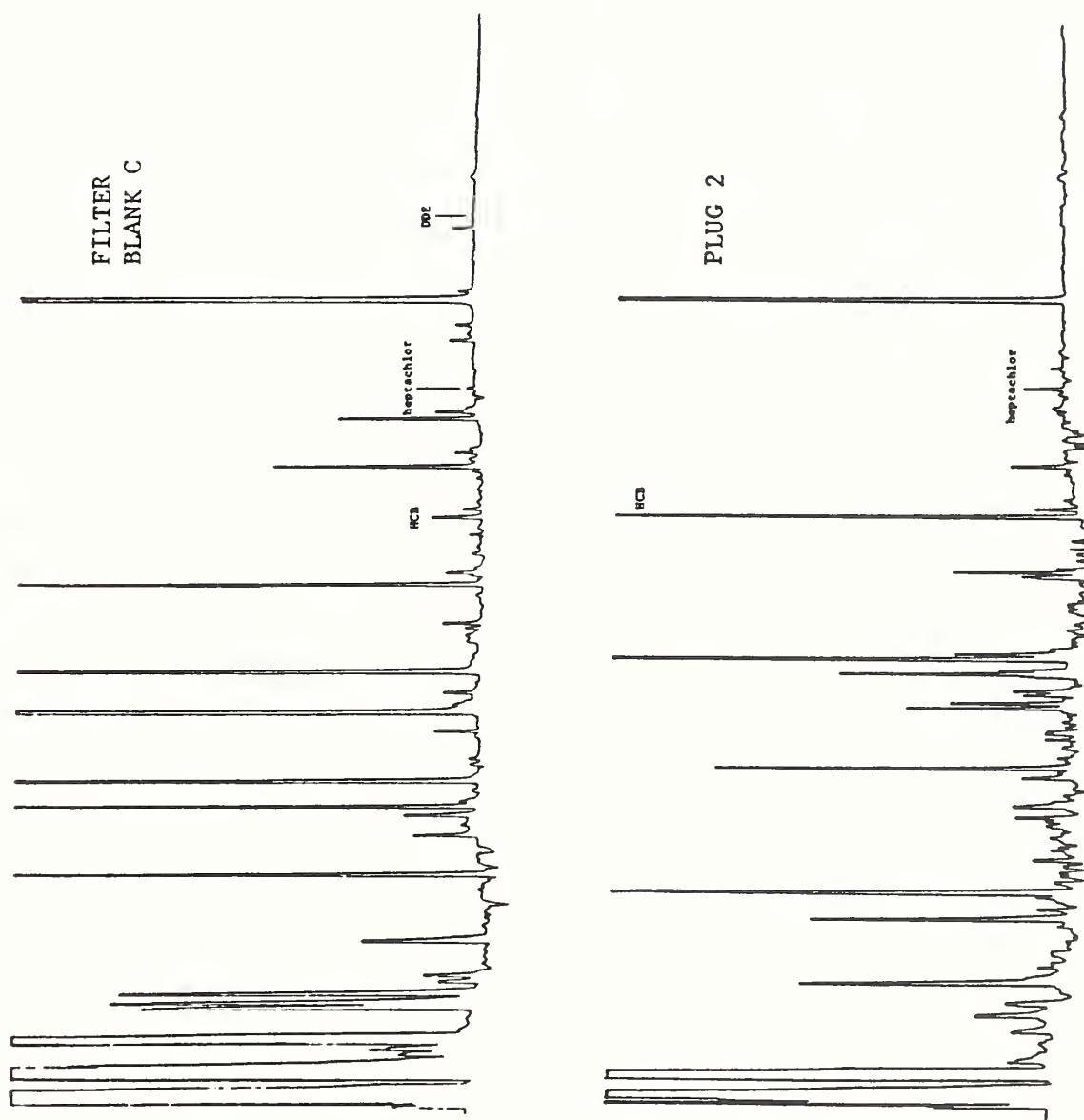


Figure 12. GC-ECD chromatogram of the non-polar (PCB) fraction for the front plug from Denver sample D4 and a mixed Aroclor 1242-1254 standard.

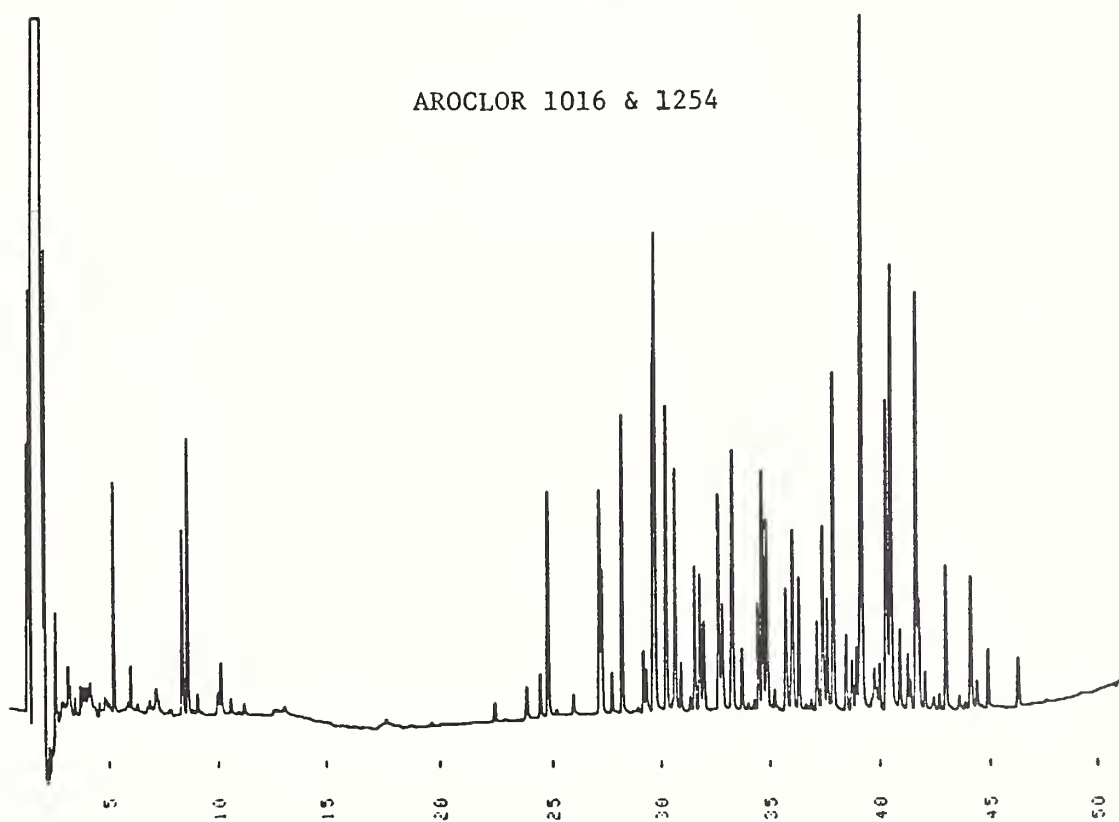
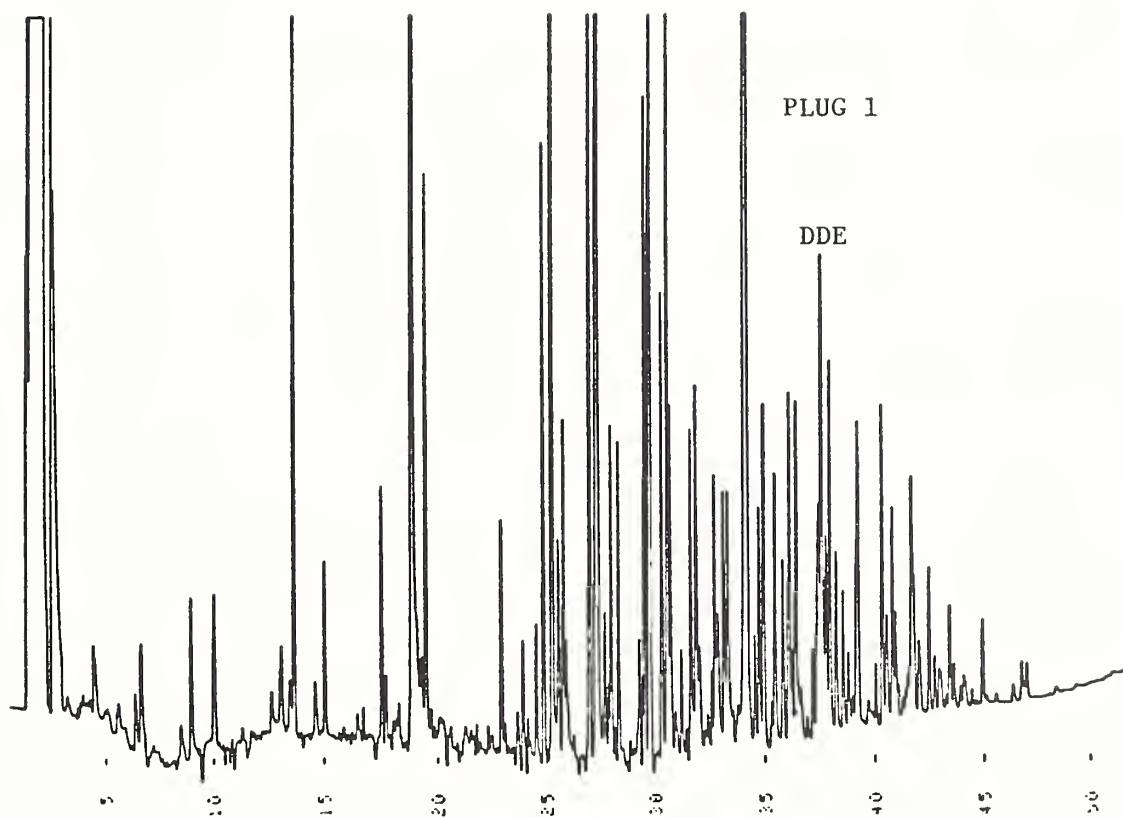


Figure 13. GC-ECD chromatograms of the non-polar (PCB) fraction for Denver sample D4.

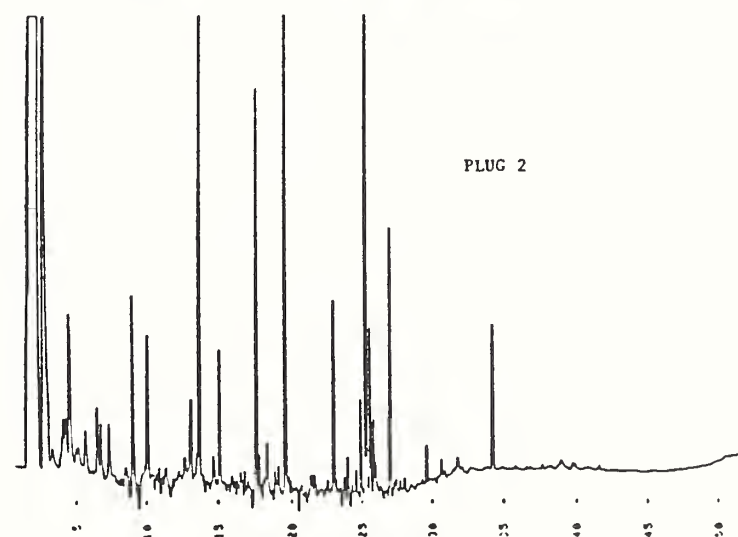
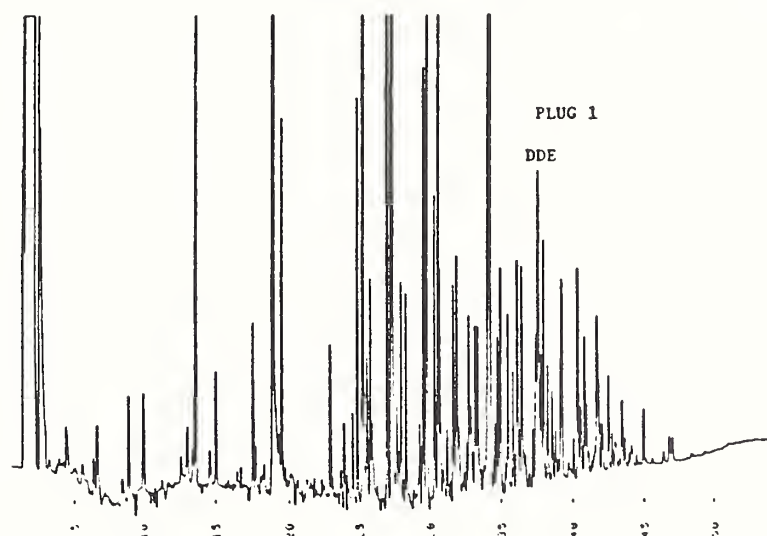
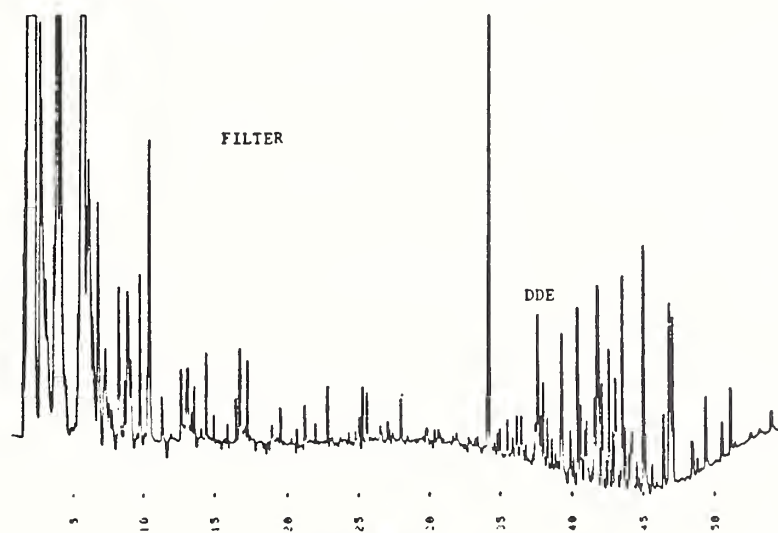


Figure 14. HLPC-fluorescence chromatograms of the polar (PAH) fraction for Denver sample D7. Peak identifications given in Table XII.

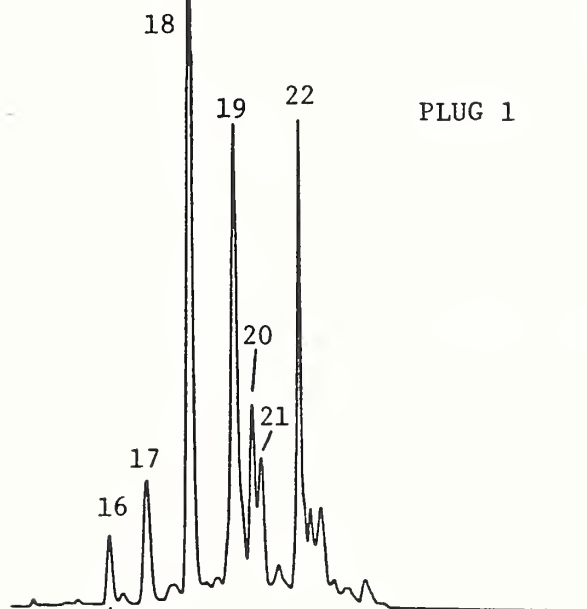
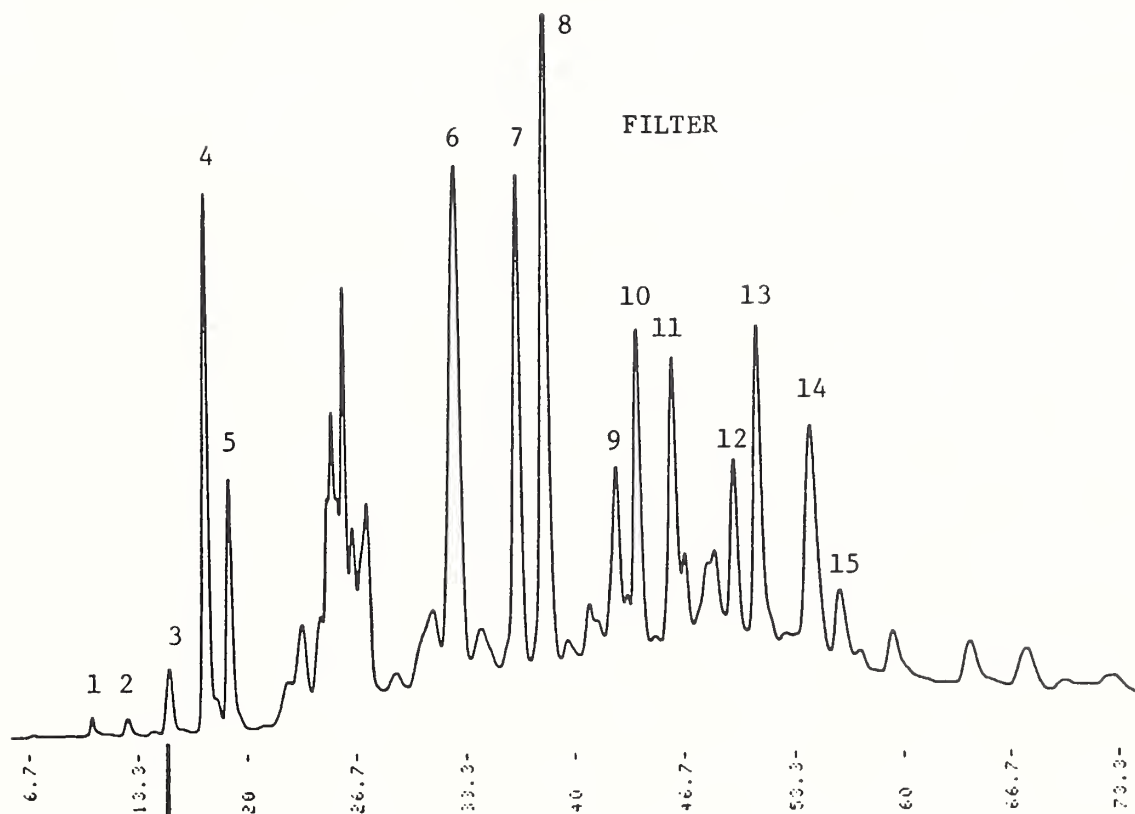


Figure 15. HLPC-fluorescence chromatograms of a mixed PAH standard and the polar fraction for Filter Blank C (January). Detector 3 times more sensitive for the filter blank than for the standard or Figure 14 chromatograms.

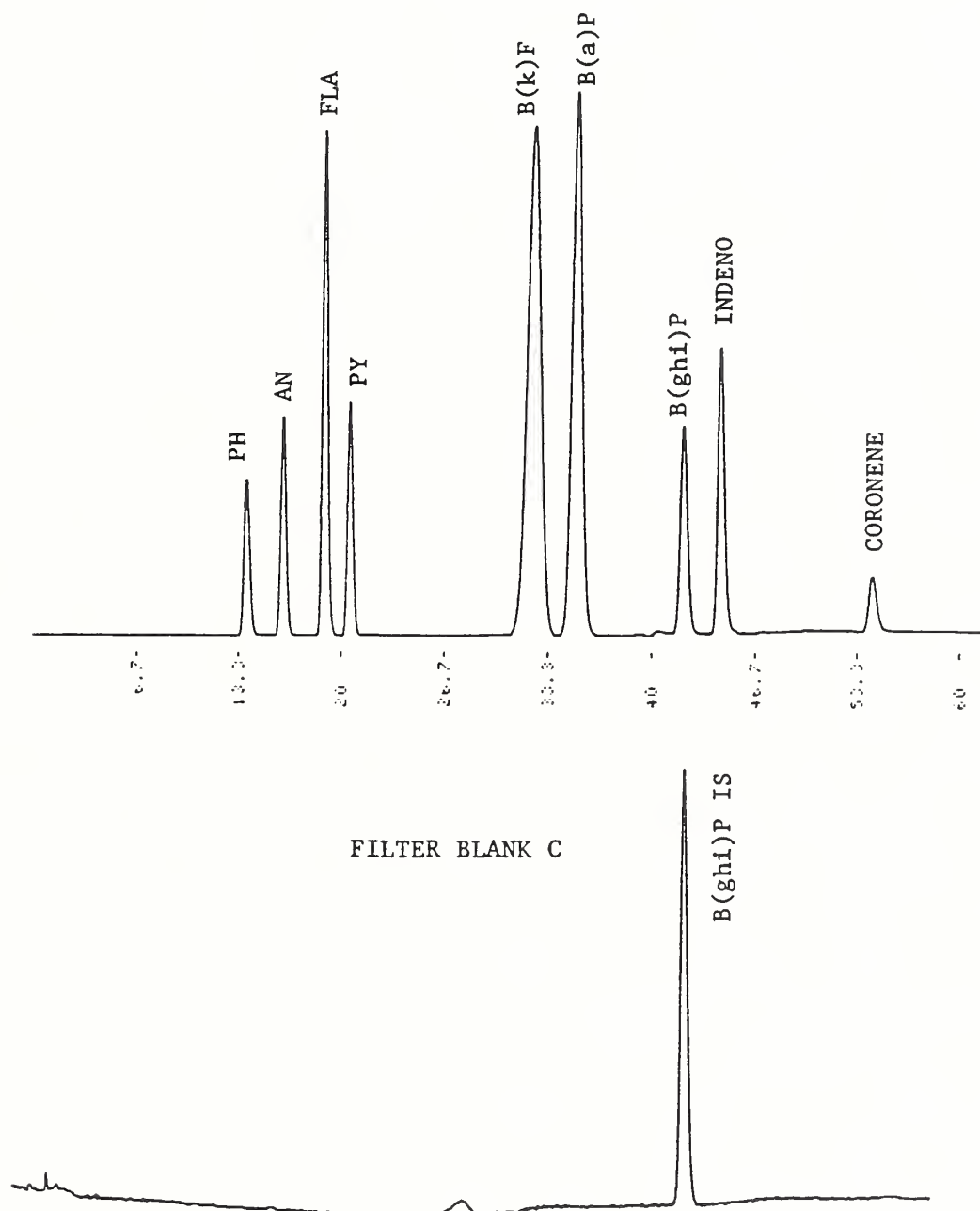


Figure 16. Plots of $\log A(\text{TSP})/F$ versus $1/T$ (Equation 2) for octadecane (C-18) and heneicosane (C-21) in Denver. 95% confidence bands for the predicted lines are included.

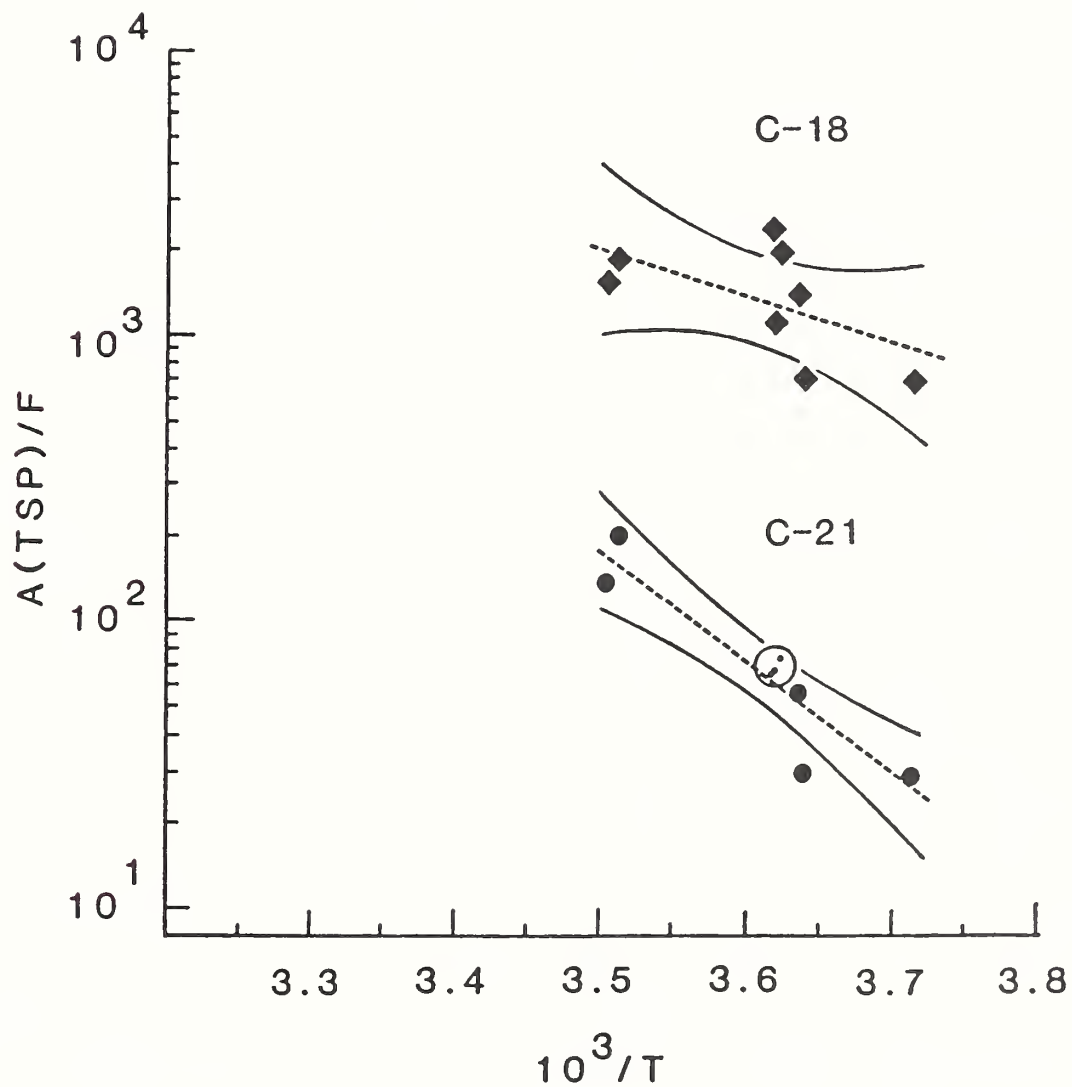




Figure 17. Plots of $\log A(\text{TSP})/F$ versus $1/T$ (Equation 2) for the organochlorine pesticides in Denver. 95% confidence bands for the predicted lines are included.

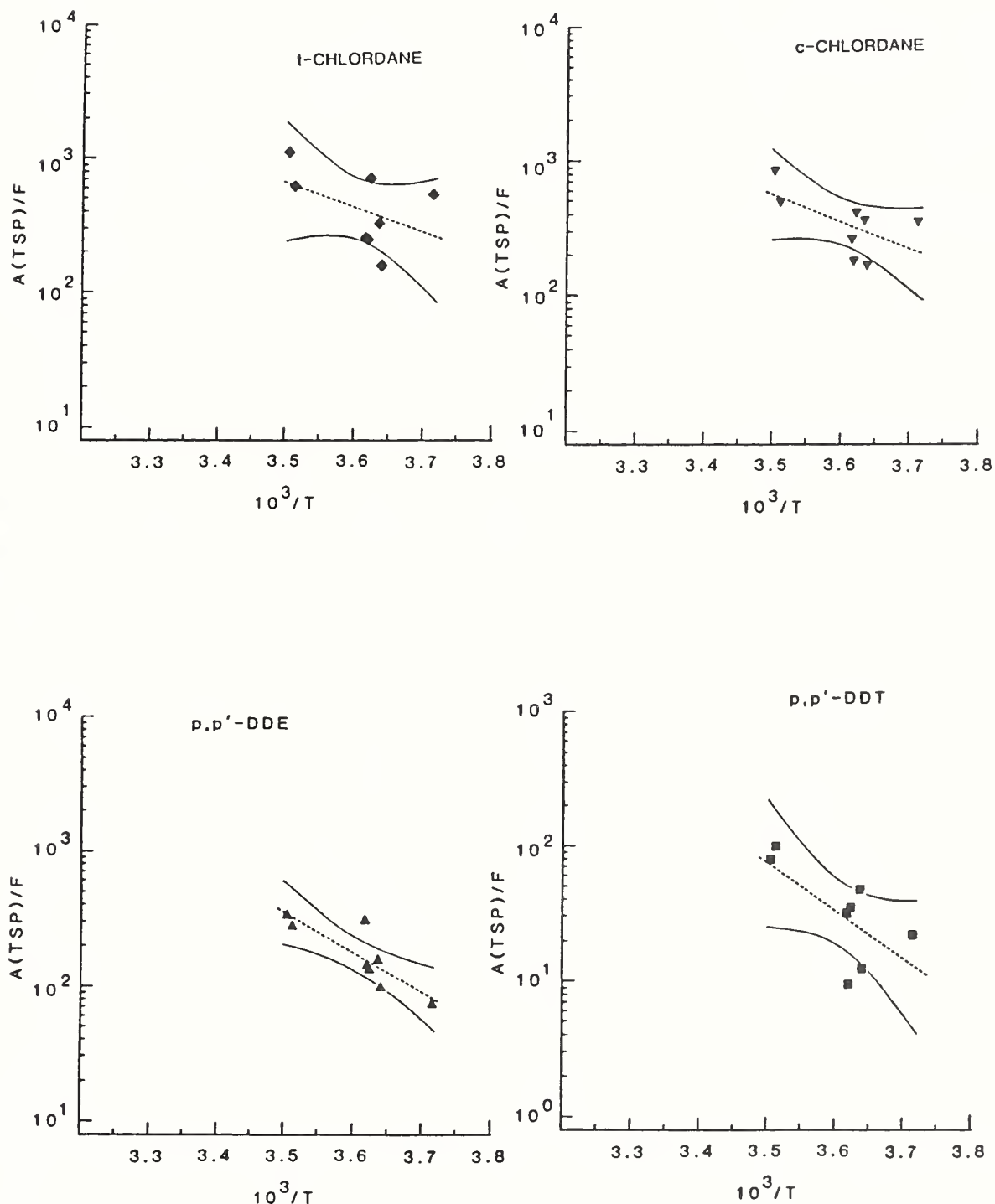


Figure 18. Plots of $\log A(\text{TSP})/F$ versus $1/T$ (Equation 2) for phenanthrene (PH), fluoranthene (FLA), and pyrene (PY) in Denver. 95% confidence bands for the predicted lines are included.

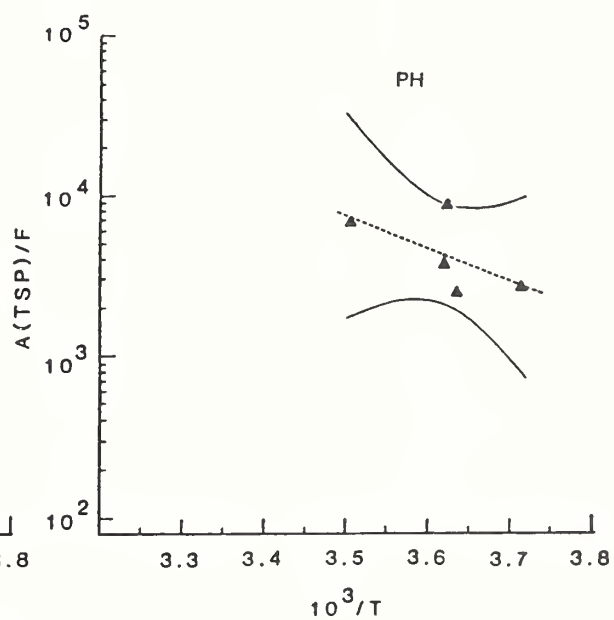
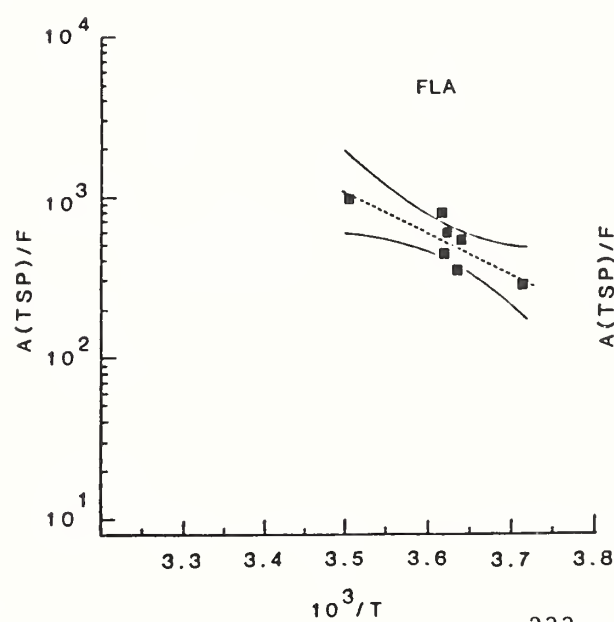
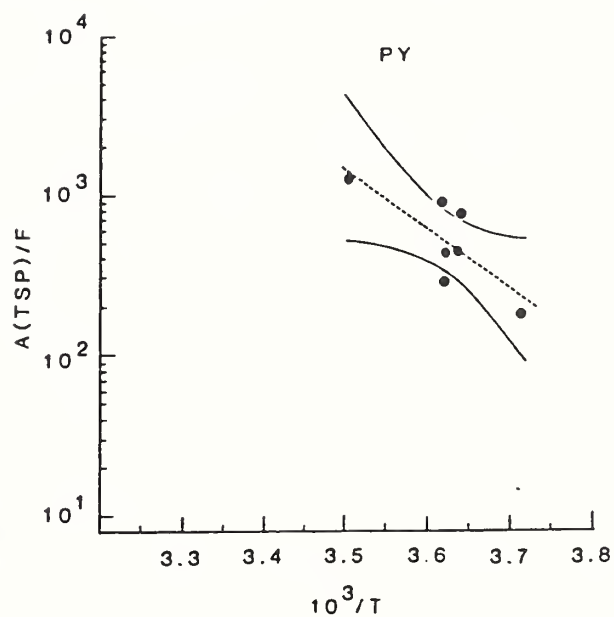


Figure 19. Plots of $\log A(TSP)/F$ versus $1/T$ (Equation 2) for some Aroclor 1254 region PCB congeners in Denver. 95% confidence bands for the predicted lines are included. Congener identifications given in Table XI.

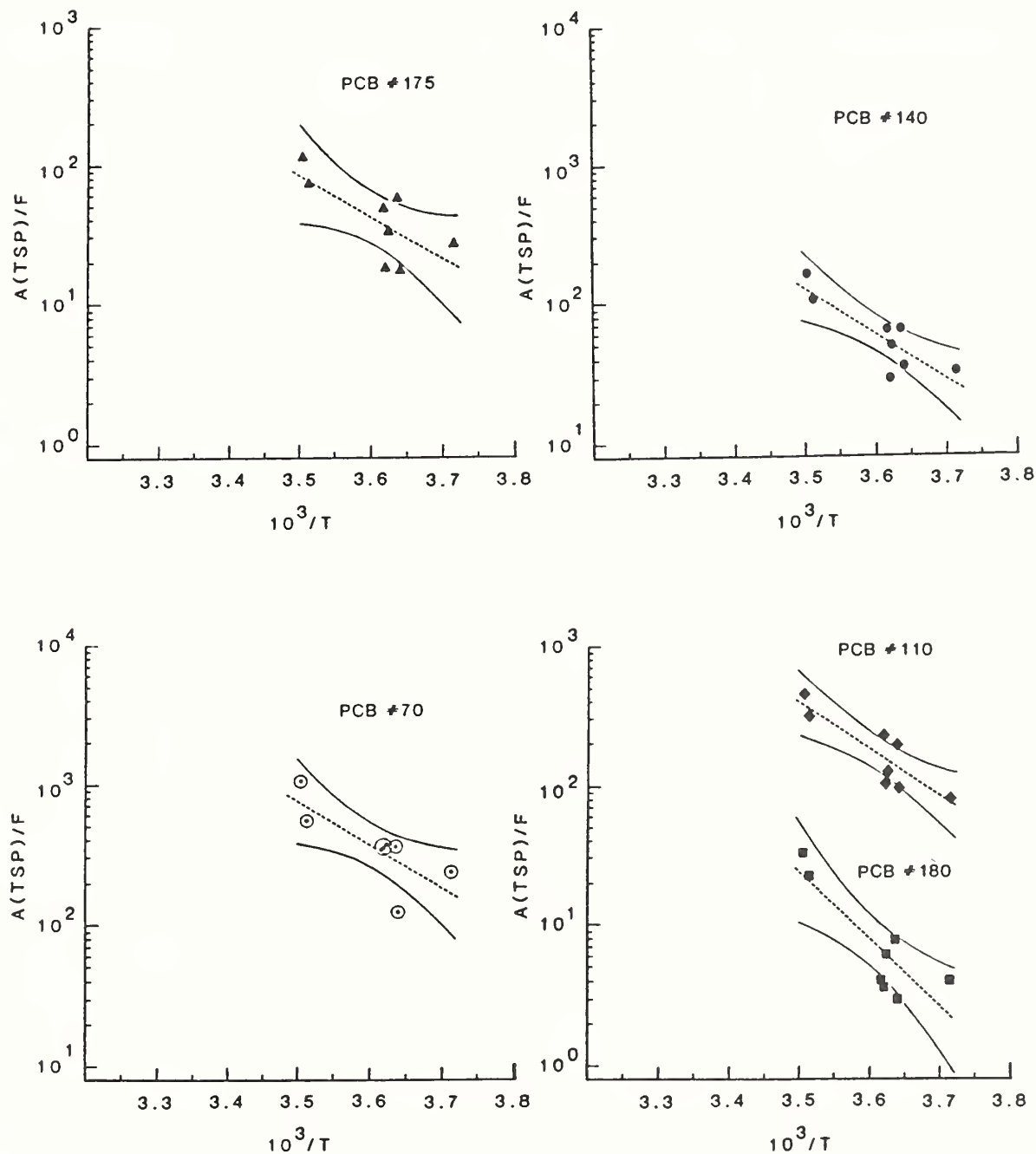


Figure 20. Plot of $\log A(\text{TSP})/F$ at 5°C versus p_L° (Equation 5) for the n-alkanes. 95% confidence limits for the predicted points, derived from the Equation 2 plots, are shown. 1 = C-18, 2 = C-19, 3 = C-20, 4 = C-21, 5 = C-22, 6 = C-23.

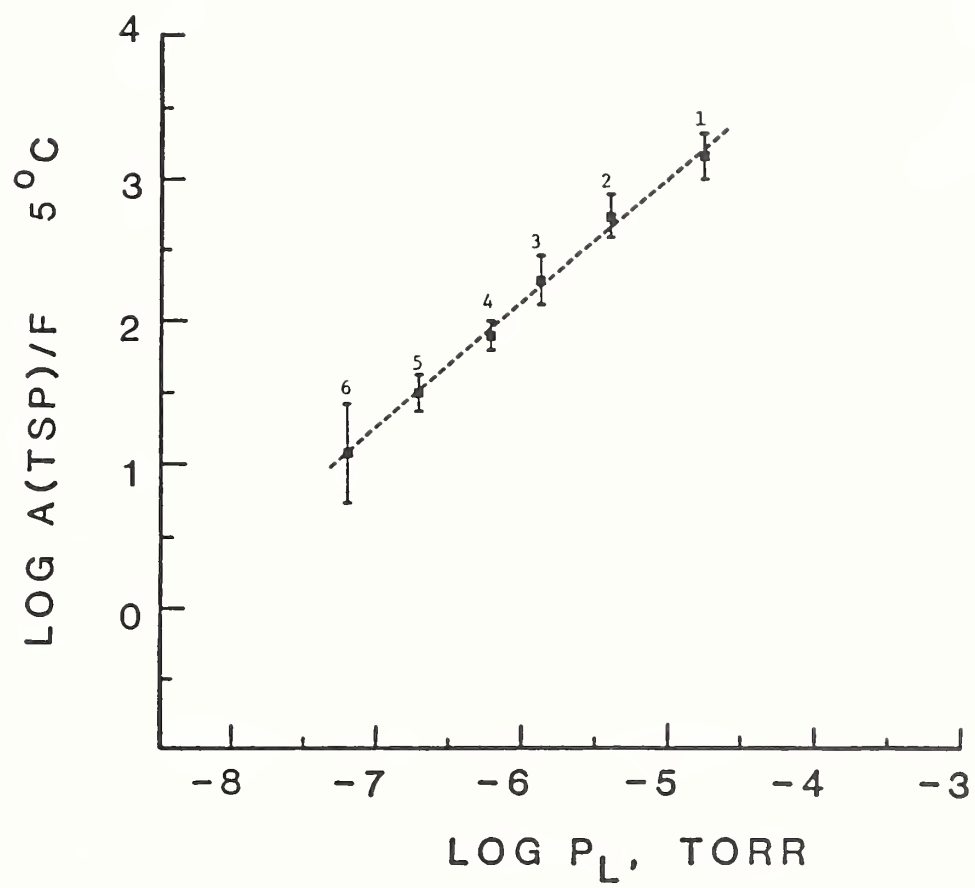


Figure 21. Plot of $\log A(\text{TSP})/F$ at 5°C versus p_L^{O} (Equation 5) for the organochlorine pesticides. 95% confidence limits for the predicted points, derived from the Equation 2 plots, are shown.

7 = trans-chlordanes, 8 = cis-chlordanes,
9 = p,p'-DDE, 10 = p,p'-DDT.

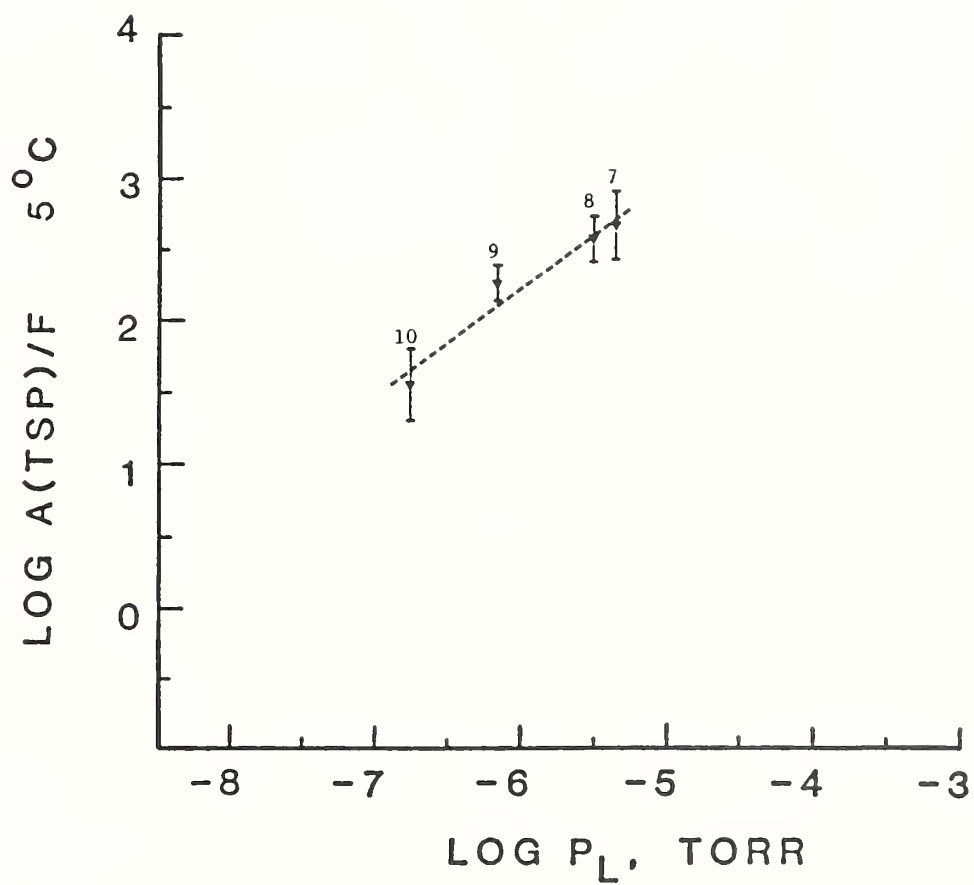


Figure 22. Plot of $\log A(\text{TSP})/F$ at 5°C versus p_L° (Equation 5) for the PAH. 95% confidence limits for the predicted points, derived from the Equation 2 plots, are shown.

11 = phenanthrene, 12 = pyrene, and 13 = fluoranthene.

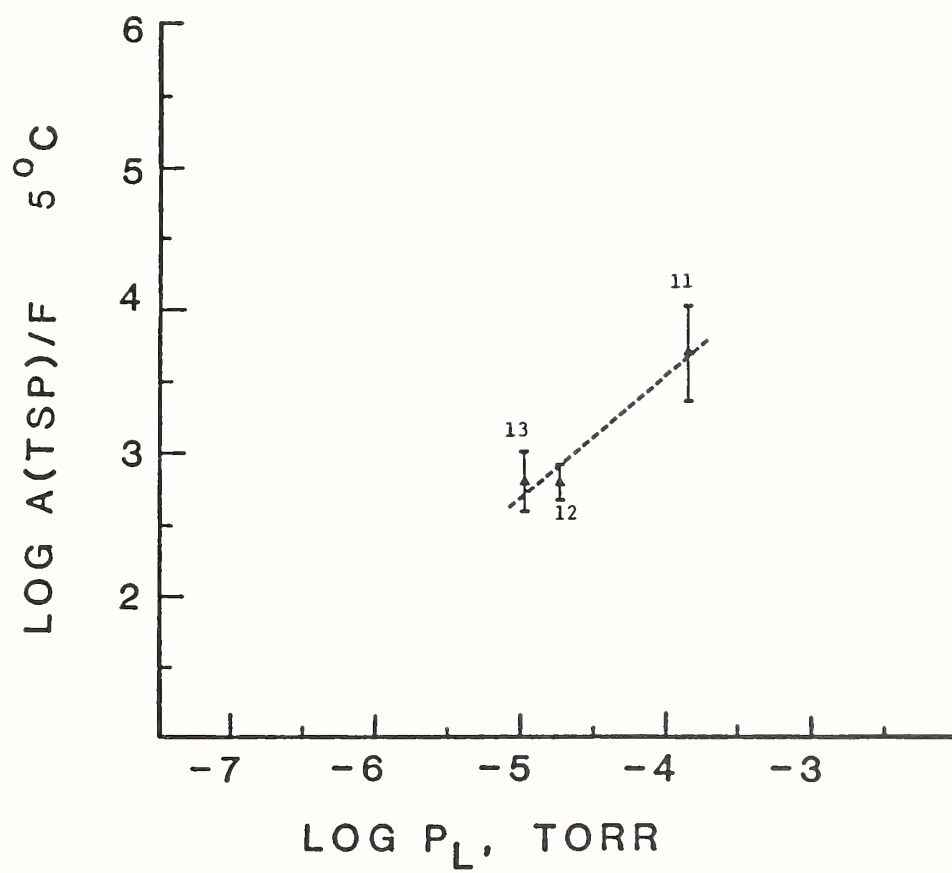


Figure 23. Plot of $\log A(\text{TSP})/F$ at 5°C versus p_L° (Equation 5) for selected congeners in the Aroclor 1254 region. 95% confidence limits for the predicted points, derived from the Equation 2 plots, are shown.

14 = PCB #70, 15 = PCB #66, 16 = PCB #101,
17 = PCB #110, 18 = PCB #82, 19 = PCB #108 + 118
+ 149, 20 = PCB #146, 21 = PCB #153, 22 = PCB
#175, 23 = PCB #180. Congener structural
identifications given in Table XI.

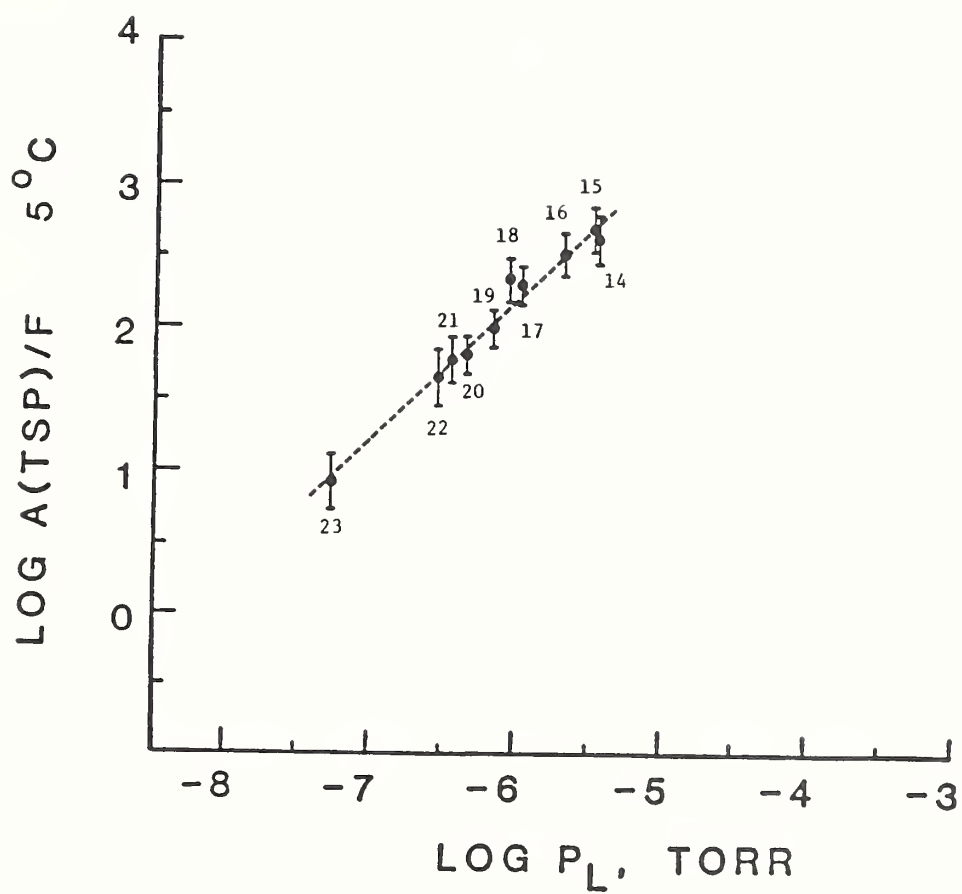


Figure 24. Replot of figure 23 showing the 95% confidence bands on the predicted line, and the position of Aroclor 1254 (total PCB, point 24) in relation to the line defined by the individual congeners.

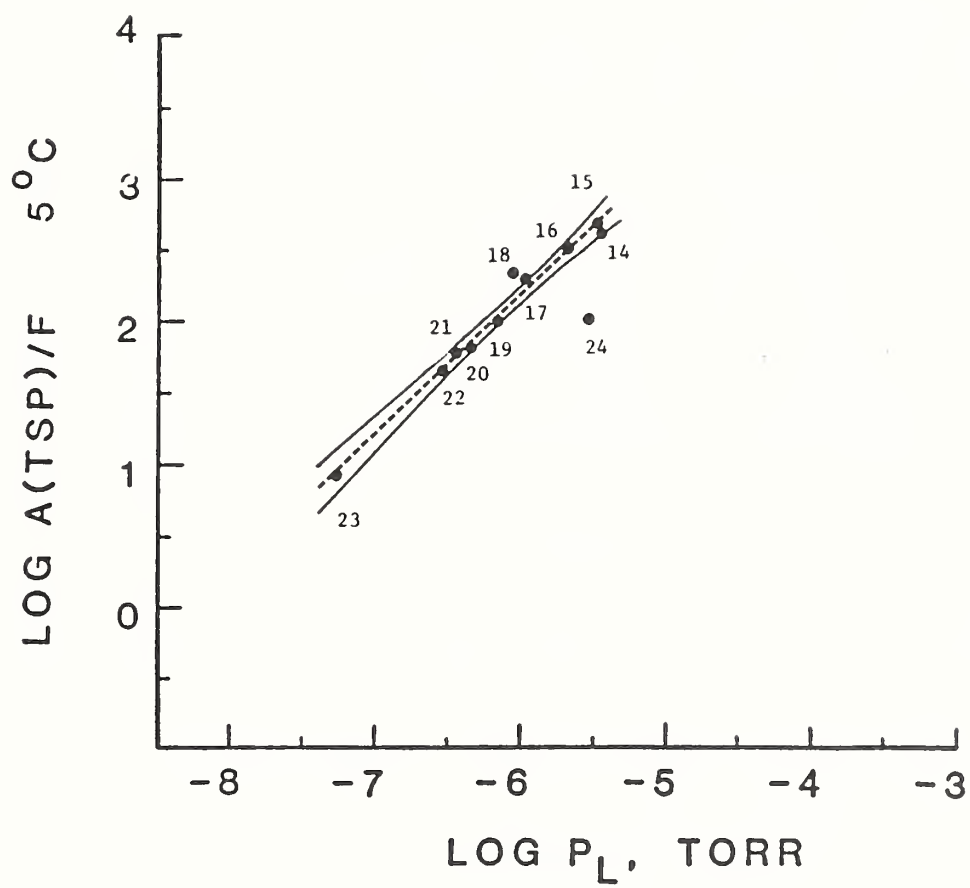


Figure 25. Plot of $\log A(\text{TSP})/F$ at 5°C versus p_L° (Equation 5) using combined data from the four SOC classes.

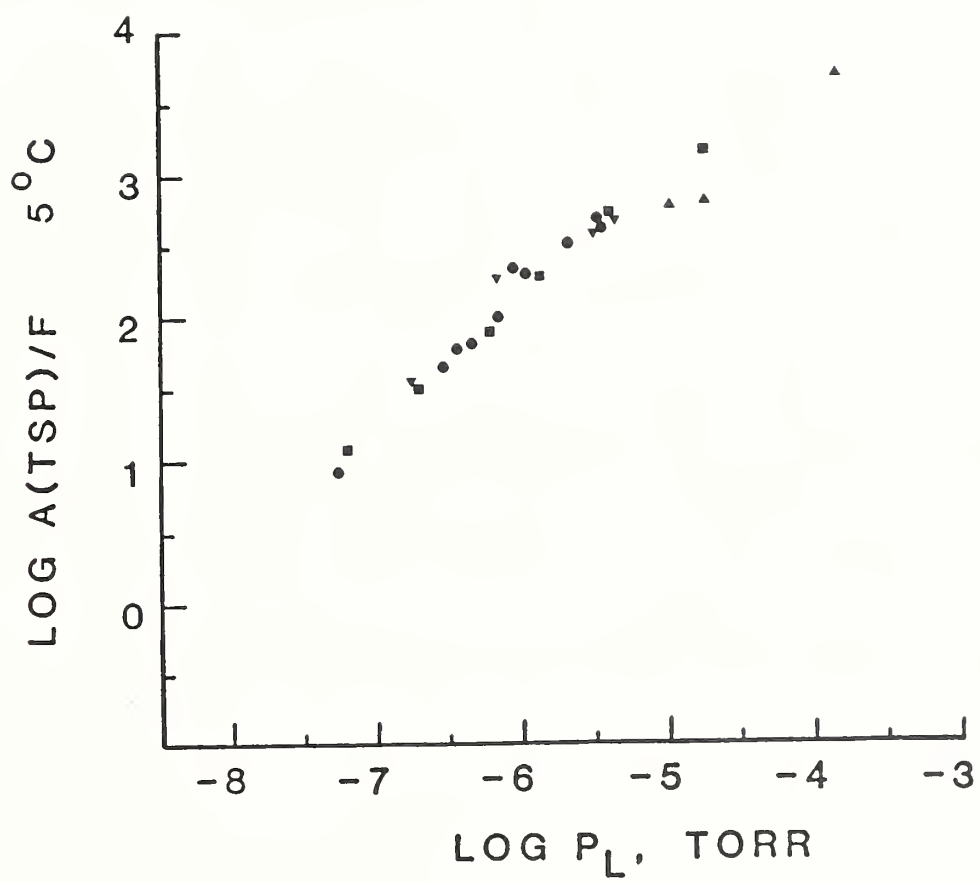
n-alkane = ■

pesticide = ▼

PAH = ▲

PCB congeners = ●

Compound identifications given in Figures 20-23.



APPENDIX A

Relationship Between Junge's Equation 3 and Yamasaki's Equation 2.

Assume that Φ , the fraction of aerosol-bound SOC, is equal to the fraction of filter-retained SOC:

$$\text{Equation 3: } \Phi = F/(A + F) = c\theta/(p^0 + c\theta)$$

$$1 + A/F = 1 + p^0/c\theta, \text{ or } A/F = p^0/c\theta$$

θ is the surface area of suspended particulate matter per cubic cm air, and is therefore $= k(\text{TSP})$:

$$A/F = p^0/ck(\text{TSP})$$

$$\text{Log } A(\text{TSP})/F = \text{Log } p^0 - \text{Log } ck$$

The temperature dependence of p^0 over the range where the heat of vaporization can be considered approximately constant is:

$$\text{Log } p^0 = m'/T + b'$$

Combining these last two equations:

$$\text{Log } A(\text{TSP})/F = m'/T + b' - \text{Log } ck$$

Setting $m = m'$ and $b = b' - \text{Log } ck$ gives Equation 2.

$$\text{Log } A(\text{TSP})/F = m/T + b$$

Note that, in the case of physical adsorption, the slope (m) of Equation 2 is the same as the slope (m') of $\text{Log } p^0$ vs $1/T$.

